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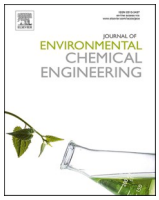

# A review on slow-release fertilizer: Nutrient release mechanism and agricultural sustainability

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ABSTRACT

The increasing need for food to support the growing population has led to the widespread use of synthetic fertilizers in the agricultural sector around the world. Most of these conventional fertilizers are inefficient as they are readily water-soluble and quickly dissolve in the irrigation water or soil moisture, yielding excessive concentrations of the nutrients in the root zone, which the plants cannot uptake. Traditional fertilizers thus cause excess nutrients in the soil that harm the environment through processes like surface run-off, denitrification, volatilization, and nutrient loss via leaching, ultimately affecting human health directly and indirectly. Slow-release fertilizers offer a promising solution to address these issues. They allow for precise control over the release of chemical contents of fertilizers, improving nutrient use efficiency and reducing environmental pollution. The controlled chemical contents of the fertilizers can promote sustainable agriculture and enhance agricultural productivity. These fertilizers are ideally biodegradable, reducing emissions and toxicity. They must possess a high water-holding capacity, promote soil microorganisms' growth, enhance the yield and quality of agricultural products. This review provides a comprehensive overview of the various slow-release fertilizer compositions, preparation techniques including their advantages and disadvantages. This study also discusses the impact of organic, inorganic, and hydrogel-based fertilizers on nutrient-release behaviors. Parameters influencing the slow-release pattern such as temperature, pH, soil texture, coating thickness, microbial activity, and soil moisture have also been discussed. This review article provides a comprehensive and up-to-date overview of the latest advancements in slow and sustained-release fertilizer for modern agriculture and its future potential.

## 1. Introduction

Due to the world's growing population, the global food demand will likely double by 2050 [1,2]. At the same time, high population growth is pushing for rapid urbanization; as a result, arable land and water resources are dwindling. Thus, there is a considerable need to ramp up agricultural productivity to meet the global food demand. Globally, annual crop yield exceeds three billion tons; 187 million tons of fertilizers are required to fulfill the agricultural demand [3]. Around 815 million people are underfed globally, and it is expected that by 2050, an additional two billion people will be added to this group [3]. Agriculture is the backbone of the economy for many developing nations pushing ahead for reforms to make agriculture a profitable venture[4,5]. One of the critical determinants of agricultural productivity is the adequate provision of quality fertilizers that supply nutrients essential for plant growth and crop yield [5,6]. Thus, the importance of quality and effective fertilizers can never be underestimated.

Simply put, fertilizers are externally supplied nutrients for crops to grow. Fertilizer is naturally required to be added to the agricultural field to replenish the nutrients removed from the harvest. However, the modern-day requirements of fertilizers are beyond simply replenishing nutrients alone. The specific yield of crops (crop yield per unit land area) needs to be maximized to meet the enormous demand for food while the arable land area is dwindling. Such a target is impossible to be fulfilled unless fertilizers are heavily used to boost the quantity and quality of crop production [7]. The famous Law of the Minimum by Liebig in 1843 states, "Crop yields are proportional to the amount of the most limiting nutrient." Plant nutrients have specific and essential functions in plant

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metabolism; one cannot replace the other if there is any deficiency in one of the nutrients [8]. For the maximization of yield and to avoid a nutrient shortage, a balanced provision of all the nutrients to the plants is required. While primary nutrients such as nitrogen, phosphorus, and potassium are regularly required, the other nutrients, such as secondary nutrients like magnesium, calcium, and sulfur, and trace nutrients such as iron, manganese, etc., are not to be supplemented regularly. Out of all the primary nutrients, nitrogen has been observed to be the most limiting factor affecting crop yield, while the other two are primarily linked with crop quality. Nitrogen is thus the most critical primary nutrient, accounting for approximately more than half of total consumption [9]. Nitrogen requires more frequent replenishment than phosphorus and potassium fertilizers.

Three different fertilizers are generally used– bio, natural or organic, and chemical. While organic and biofertilizers have biological origins, chemical fertilizers, also known as inorganic or synthetic fertilizers, are produced from several mineral and inorganic resources through chemical processing in fertilizer. Chemical fertilizers contain nitrogen, phosphorus, and potassium as their main ingredients. Bio, organic, and mineral fertilizers (chemical fertilizers) deliver the same inorganic molecules that the plants can utilize as nutrients. Biofertilizers include living microorganisms that enhance plant growth and nutrient uptake. These substances are alternatively referred to as microbial fertilizers or microbial inoculants. Bio-fertilizers consist of biological constituents, comprising living organisms that facilitate the synthesis of atmospheric plant nutrients inside the soil or create an optimal environment for plant growth within the soil. Organic fertilizers add organic content to the soil and thus support the beneficial microbes growing in the root zone of the plants. These microbes decompose the organic fertilizers to release the minerals that the plants take up as nutrients to support their growth [10]. Thus, the microbe content in the soil is a determinant of the efficiency of such organic fertilizers. The soil's microbial content varies depending on the environmental conditions at a particular place. Thus, the nutrient supply to the plants using organic fertilizers, dependent on environmental and climatic factors, is inconsistent with the quality and quantity. Plant productivity achieved by organic and bio-fertilizers is low compared to mineral fertilizers. Therefore, although claimed to be environmentally and ecologically sustainable, organic and bio-fertilizers suffer from several drawbacks, such as low concentration of nutrients, leading to the need for large amounts of organic and bio-fertilizer to be transported and stored; inconsistent quality depending upon the source; low availability of nutrients, etc. Similarly, several management approaches, such as biochars, compost, organic manures, mulching, cover crops, crop residues, zero-tillage, agro-forestry, and crop diversification, are commonly recommended to improve soil carbon content while also managing soil nutrients[11,12]. The application of biochar also resulted in secondary benefits such as increased fertilizer efficiency and nutrient savings [13].

At present, chemical-based fertilizers dominate the fertilizer market. Proponents of chemical fertilizers argue that these fertilizers help maximize the crop's quality and yield because their use makes it often possible to deliver nutrients in optimal and balanced proportions commensurate with the demands of a specific crop. Chemical fertilizers are used indiscriminately in agricultural fields to increase food production [14]. However, their long-term use has been blamed for deteriorating food quality and soil fertility [15]. Traditionally, these fertilizers are either water-soluble or liquid, and hence their use in the field is associated with several disadvantages, such as loss through leaching in the soil, as run-off from the agricultural field, and loss through volatilization [16,17]. Fertilizers and their residues in surface- and groundwater cause problems such as blue baby disease, algal growth leading to eutrophication, and deleterious effects on the aqueous and land ecosystem [18]. Nitrogen-based fertilizers or N-fertilizers can also release a greenhouse gas, nitrous oxide, from the soil into the atmosphere. Nitrogen is the most crucial nutrient for plants, so nitrogen fertilizers are essential for plant growth. It has been reported that N-fertilizer is the most frequently used fertilizer. In conventional fertilizers, urea is primarily used as a nitrogen resource.

The most frequently used form of urea is synthetic fertilizers, in pilled or granulated form. It contains 46 % nitrogen and is highly water-soluble [19]. Applying urea fertilizer in the soil leads to a sequential conversion, resulting in a nitrogen release for plant growth [20]. Urea is a stable molecule, and its half-life is around 40 years at 25 °C. Therefore, it is not spontaneously degraded in solution [21,22]. This reaction can only occur when the urea is dissolved in the water solution in the soil pores. Under this condition, urea can react with water, and the soil bacteria release the enzyme urease to unlock $NH_4^+$ from urea through mineralization. Plants can use this ammonium ion. This process is called ammonification. The reactions involved in the above-mentioned steps has been given in Fig. 1. Nitrifying bacteria convert this ammonium into nitrate ($NO_3^-$). These nitrates can be taken by plant root systems directly [1].

Similarly, the plant system can use organic nitrogen (humus) in the soil. Further, the mechanism plants use to mobilize P nutrients from the soil is carboxylate (organic anions) exudation. [24]. The presence of carboxylate significantly improves the uptake and availability of immobile phosphate nutrients for plant development. These carboxylates break apart into organic anions, which results in the release of phosphate into the soil solution by chelating iron or aluminum that is bound in metal-phosphate complexes. On the other hand, carboxylates and phosphorus compete for the same adsorption site on metal hydrous oxides in soil, resulting in the displacement of phosphorus. The phosphatase enzyme is also involved in this process; however, it is unclear how it is released [25]. The phosphatase enzyme hydrolyzes organic P to promote the mobilization of that substance. Plants may use specialized transporters to absorb organic P after the hydrolysis process. Carboxylates are capable of mobilizing both inorganic and organic P. In addition, some transporters may allow plants to absorb inorganic P directly. Some cations, notably Fe (iron) and other micronutrients that bind with P, also chelate via carboxylate. The reduction process begins when this chelated Fe (iron) moves to the root's surface. Fig. 2 explains how nitrogen fertilizers and carboxylates (and other exudates) affect the mobilization of both inorganic ($P_i$) and organic ($P_o$) phosphate in the soil work. The plants' root also has this chelated Fe (iron) absorption through the $Fe^{2+}$ transporter. Other micronutrients such as copper (Cu), zinc (Zn), and manganese (Mn) are also transported by this transporter, and they may also be mobilized by carboxylates in soil [26]. In addition, plants absorb the minerals from the soil by respirationally releasing $CO_2$ via their roots and pumping $H^+$ into the ground. The $H_2O$ and released $CO_2$ combine to make $H_2CO_3$. Additionally, $H_2CO_3$ dissociates to liberate $H^+$ ions. The released $H^+$ ions in the soil solution help neutralize the negative charge of soil particles, causing a release of mineral cations into the soil solution [27]. The root system absorbs these released cations. While plants need large quantities of macronutrients like N, P, and

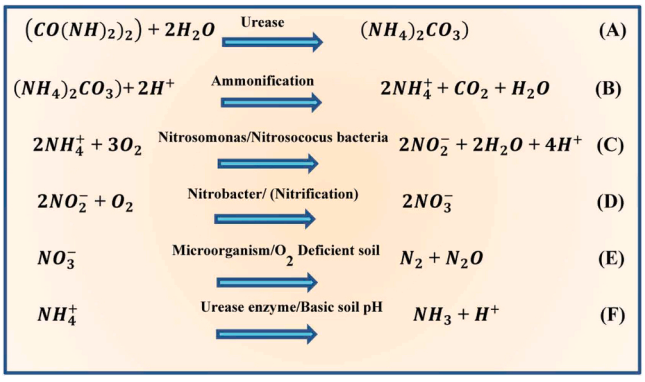
$(CO(NH)_2) + 2H_2O$ Urease $(NH_4)_2CO_3$ (A)
$(NH_4)_2CO_3 + 2H^+$ Ammonification $2NH_4^+ + CO_2 + H_2O$ (B)
$2NH_4^+ + 3O_2$ Nitrosomonas/Nitrosococus bacteria $2NO_2^- + 2H_2O + 4H^+$ (C)
$2NO_2^- + O_2$ Nitrobacter/ (Nitrification) $2NO_3^-$ (D)
$NO_3^-$ Microorganism/$O_2$ Deficient soil $N_2 + N_2O$ (E)
$NH_4^+$ Urease enzyme/Basic soil pH $NH_3 + H^+$ (F)

**Fig. 1.** Simple nitrogen cycle in the soil showing fertilizer conversion from one form to another (adapted from [23]).

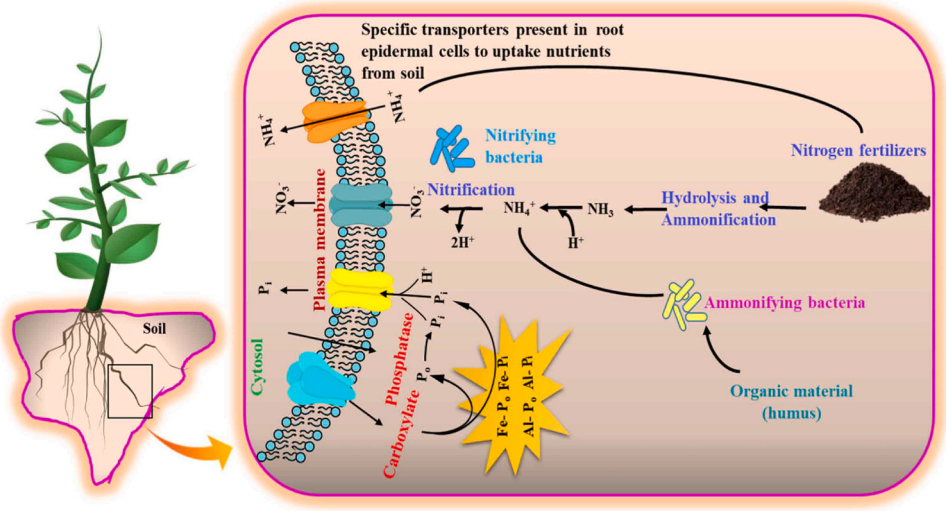


**Fig. 2.** Mechanism of nitrogen fertilizers and carboxylates (and other exudates) on inorganic ($P_i$) and organic P ($P_o$) mobilization in soil.

K (nitrogen, phosphorus, and potassium), they only require modest amounts of these minerals. Plants have special transporters for absorbing these macronutrients found in the soil.

In the soil, ammonium ion gets converted into nitrite and nitrate ions via the nitrification process with the help of Nitrosomonas and Nitrobacter bacteria residing within the soil. These reactions produce the required nutrients for plant growth [23] and release excess nitrogenous compounds into the soil. They are highly soluble and mobile species and can produce nutrient-laden run-off from agricultural fields, often resulting in large-scale pollution in the surface water bodies. Phosphate is less soluble than nitrate and can also be transported through run-off. Phosphate loss due to erosion is common in nature. Phosphate in the surface run-off can also cause algal growth and unwanted plant growth, often in lakes, estuaries, and freshwater streams [28]. Thus, increased use of chemical fertilizers causes loss in soil fertility and is also associated with significant water pollution when lost into the environment as leachate and runoff, leading to far-reaching effects on the environment [29]. Also, a significant proportion of the fertilizers applied in the field are wasted as it is lost through leaching and runoff; a vast amount of nitrogen (N), phosphorous (P), and potassium (K) in the form of $NH_3$, $P_2O_5$, and $K_2O$ applied in the field are lost by 40 %–70 %, 80 %–90 %, and 50 %–90 % respectively, through chemical hydrolysis, photodegradation, and leaching [30].

Slow-release fertilizer should be coated with a biodegradable organic or inorganic polymer that slows the fertilizer's release rate and improves crop yields per unit of fertilizer used. Thus, applying slow-release fertilizers is considered a best management practice (BMP) tool for crop production. Therefore, the researchers focus on developing slow-release fertilizer (SRF) with a low cost and high efficiency, which provides a sustained release of fertilizer to the soil commensurate with the plant's

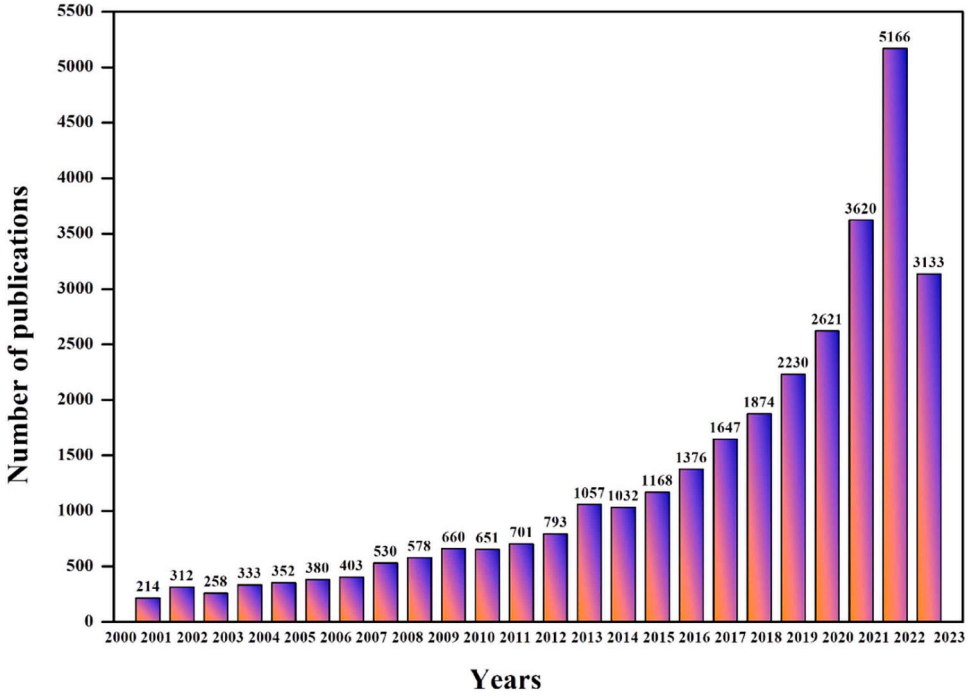


**Fig. 3.** The number of publications on slow-release fertilizers for agriculture during the last 20 years. Data source: Science Direct, Access date: 20 August 2023, Time:11:30 pm.

demands. SRFs economize fertilizer consumption by limiting leaching and loss with run-off. It decreases the environmental impact and, at the same time, enhances crop yield [31]. The first-ever SRFs were reported during the 1920s, although their market did not grow until the 1960s. The SRF industry started to evolve in the 21st century, and its annual growth rate was 6.5 % from 2014 to 2019 [32]. Therefore, it is evident that SRFs have already gained greater attention from farmers for replacing conventional fertilizers in the last few years. As can be observed from Fig. 3, the number of articles published in Science Direct (Access date: 20 August 2023, Time:11:30 pm) searched with the term ''slow-release fertilizer for agriculture'' has grown exponentially over the last 20 years. In 2022, around four thousand documents related to SRFs were listed; the data speaks of the researchers' significant attention to the development, application, and performance of SRFs in the agricultural field. There are natural and synthetic forms of SRFs. The ideal difference between slow-release fertilizers (SRFs) created from natural and synthetic materials is that SRFs made from natural material deliver nutrients to the soil as they naturally break down and decompose. Additionally, synthetic material fertilizers decompose in the presence of water, heat, sunlight, or microorganisms [33]. Figs. 4 and 5 show the mechanism by which slow-release fertilizers work. The primary research job for the coming time is to advance the competence of nutrient uptake, specifically, the nitrogen consumption efficiency of plant roots [34]. Often, the fertilizers are coated with appropriate material to convert it to SRF, which essentially controls the release rate of nutrients into the soil by reducing the solubility of the fertilizer. The coating on the fertilizers generally forms a physical barrier that breaks down slowly when applied to soil, resulting in a slower rate of disintegration of the fertilizer in water [35]. This process helps prevent unwanted fertilizer loss by making most fertilizer available to the plants on time during their growth. Fig. 6 summarizes the general mechanism of SRFs, their benefits in agriculture, and a few necessary specifications. Due to their benefits, there is a growing market trend toward using more eco-friendly SRFs. Furthermore, less effort is required with this slow-release fertilizer, making it an ideal choice for plantations, and it was found that the physical features of the substance employed to coat the SRFs were the driving force behind the nutrient release [36].

SRF formulations reduce the loss of nutrients through leaching and run-off during the irrigation of the agricultural field compared to chemical fertilizers by allowing dissolution only through degradation by microbial action, hydrolysis, and photolysis [37]. The SRF formulations

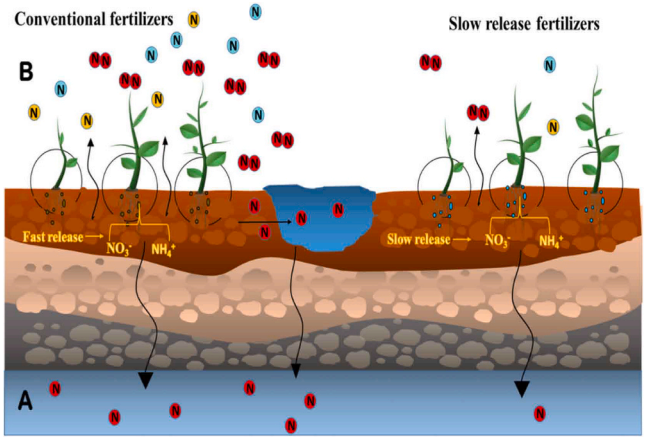


**Fig. 4.** The slow-release fertilizers supply nutrients that fulfill the plant's demand to give optimal growth and reduce leaching. (A) leaching of nitrogen from the soil into water bodies, either into groundwater or above-ground water, including rivers, lakes, and oceans. (B) Some microorganisms can convert nitrogen fertilizers into different types of nitrogen gases in the atmosphere in the form of greenhouse gases. In the case of slow-release fertilizers, the leaching and conversion of greenhouse gases are less than in conventional fertilizers.

can be particularly effective in arid regions where their use would help in delivering the required dosage of nutrients to the plant roots and, at the same time, would ensure microbial safety and economic sustainability by promoting biodegradability, water retention capacity and controlled release of fertilizers [38]. The capability of SRFs to release nutrients at a controlled rate can enable them to deliver nutrients to the plant root for a whole cultivation cycle or over multiple cycles together. The controlled release also ensures no disproportionate nutrient delivery in the root zones. Thus, on the one hand, it ensures adequate delivery of nutrients, and on the other hand, it leads to substantial cost savings by reducing the frequency of fertilizer additions to the field and related labor costs. Currently, various SRFs have been synthesized, viz., synthetic (polymer-coated and encapsulated material) and nonsynthetic (cellulose, chitosan, starch) [39]. However, existing SRFs generally do not have a specific size, so plants cannot wholly uptake them. Besides this, SRFs do not show a particular pattern for the release of nutrients. Therefore, a gap is generated between the rate of supply of nutrients released from SRFs and the absorption of nutrients by the plants. The present review paper aims to provide comprehensive knowledge in this area, from the fundamentals to the modern advancements found in the most recent literature studies on various types of organic and inorganic slow-release fertilizers for agriculture, their usages, their uses process of synthesis, and mechanisms of action. This study would help enhance the knowledge of enduring research on delivering different types of slow--release fertilizer to plant roots. The keywords included soil fertilization, nutrient uptake, release mechanism, biopolymer encapsulated fertilizer, hydrogel-based fertilizer, synthetic coated fertilizer, hydrophobic film coated fertilizer, ammonia volatilization, nutrient leaching, water retention, and plant growth.

## 2. The necessity of slow-release fertilizers (SRFs)

Most chemical fertilizers have high solubility and, thus, can be considered quick-release fertilizers. Out of all other chemical fertilizers, nitrogen in the form of urea is considered the poorest fertilizer as it is highly water-soluble. Plants only need a minimal quantity of food in the early stages of growth. The fertilizer provided in the early stage, which remains unused, would not be available for later development of the plant because of its water-soluble nature, which typically causes urea to wash away with run-off water. The leading causes of the low nitrogen efficiency of these fertilizers include losses due to heavy rainfall or irrigation's excessive water and leaching into natural water resources. As per equation (A) to (D) in Fig. 1, urea naturally converts to mobile nitrate in the soil. High concentrations of nitrate ions in the run-off water could pose high risks to humans and aquatic animals [23,40]. In addition to its role in water pollution, nitrogen may also be lost due to volatilization in the form of $N_2$ and $N_2O$ through full and partial denitrification processes, respectively, as per equations (E) and (F) in Fig. 1. [41]. Also, as per equation (F), ammonium-nitrogen loss is possible in alkaline soil through volatilization into ammonia gas. Nitrous oxide ($N_2O$), produced mainly from these nitrogen fertilizers, is the chemical most often cited as the cause of the loss of the ozone layer across the planet [40,42]. It is also reported as a greenhouse gas [43]. Therefore, in recent years, the scientific community has shifted its attention to finding ways to cut down the nitrogen losses associated with urea fertilizers while improving crop yield. The success of such activity would likely result in the preservation of the short- and long-term nitrogen balance on a global scale. One of the feasible solutions to this issue is to utilize smart or intelligent fertilizers, such as slow-release fertilizers or SRFs. They can not be only used for the controlled release of nitrogen but ideally can be applicable for the sustained release of different other nutrients as well. It is best to provide crops with a steady supply of nutrients by using SRFs, as their slow-release properties make them ideal for this purpose [44].

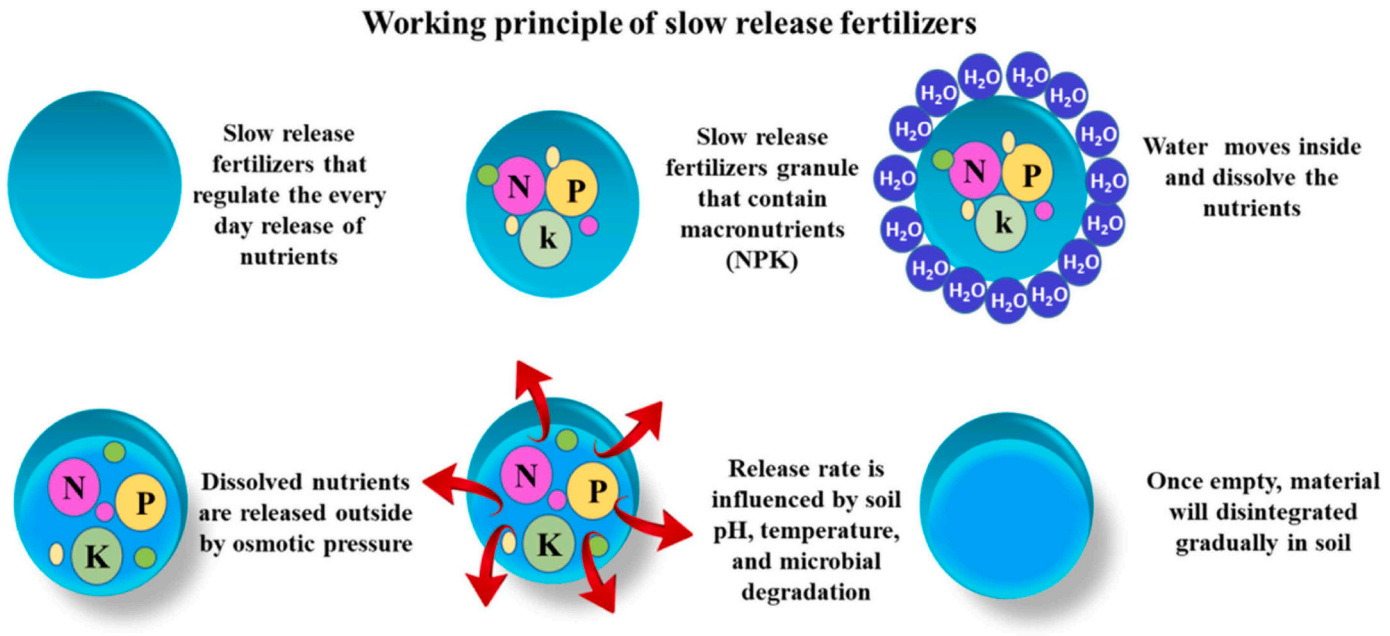
Working principle of slow release fertilizers
Slow release fertilizers that regulate the every day release of nutrients
Slow release fertilizers granule that contain macronutrients (NPK)
Water moves inside and dissolve the nutrients
Dissolved nutrients are released outside by osmotic pressure
Release rate is influenced by soil pH, temperature, and microbial degradation
Once empty, material will disintegrated gradually in soil

**Fig. 5.** Mode of action of slow-release fertilizers.

## 3. Slow-release fertilizers

Compared to conventional and quick-release fertilizers like urea, ammonium nitrates, potassium chloride, and ammonium phosphate, etc., SRFs are effective because they either limit the fertilizers' availability for absorption by the plant or considerably delay the release rate to the plant [45]. A few examples of commercially available SRFs are Nitroform ($HC[NO_2]_3$), urea-isobutyraldehyde/isobutylene diurea (IBDU), urea-formaldehyde (UF), and urea-acetaldehyde (UA) /cyclo diurea (CDU) [20]. Nitroform, sometimes also termed trinitromethane, is an inorganic slow-release fertilizer [46], while organic slow-release fertilizers include IBDU, UF, UA, CDU, etc. These slow-release fertilizers are designed to provide active nutrients slowly and steadily under varying osmotic pressures to match the plant roots' sequential nutritional needs [20,47].

The critical attributes of SRFs include:

- Slow-release fertilizers, particularly nitrogen fertilizers, should be able to decrease nutrient loss by making only a tiny proportion of the whole application in the soil to be accessible to the plants.
- They should also minimize nitrogen volatilization loss, improve harvest quality, and boost production yields.
- The efficiency of these fertilizers should be sufficient to improve the utilization of macronutrients, save energy, decrease environmental pollution, and should be economically viable.

All kinds of plants, including trees, shrubs, turf grasses, perennials, and annuals, are benefitted from SRFs. The use of SRFs should substantially reduce fertilizer requirements, thus mitigating some of the problems that might arise from over-fertilization.

### 3.1. Classification of slow-release fertilizers

According to the available literature, slow-release fertilizers may be categorized based on different attributes, such as the type of coating and the release mechanism involved. According to past research work [19, 20,35] the SRFs can be generally categorized into organic and inorganic forms as explained in Fig. 7.

### 3.2. Inorganic low solubility slow-release fertilizer

Commonly used low solubility inorganic SRFs consist of compounds with standard formula $MeNH_4PO_4.xH_2O$, where "Me'' stands for divalent cations of metals such as Fe, Zn, Mg, or Mn. This category of inorganic material has metal-based ammonium phosphates, such as magnesium ammonium phosphate ($MgNH_4PO_4$), potassium ammonium phosphate ($KNH_4PO_4$), and acidified phosphate rock. Further, partially acidulated phosphate rock, popularly known as PAPR, is also a low-solubility phosphate that can be considered a slow-release P fertilizer, mainly used in slightly acidic or light-textured soil [48].

### 3.3. Organic slow-release fertilizer

This type of SRF can be further classified into two major categories: natural and synthetic. Natural organic SRFs are plant and animal manures (cow, chicken, poultry), crop cover (also known as green manures), composts, blood meal, cottonseed meal, soybean meal, fish emulsion, etc. [49]. Since the SRF is organic, microorganisms break it down before releasing the nutrients into the soil. Therefore, the amount of nutrients released by SRFs depends on the microbiological activity of the soil, which is influenced by moisture content and temperature within the soil. Thus, natural SRFs often take longer than the required time to release the nutrients in the soil, and these nutrients may not be available when the plant most needs them. These organic SRFs may be formulated to have both micronutrients (Fe, Mg, Cu, etc.) and macronutrients (N, P, K) [50]. For nitrogen-based fertilizers, the soil's temperature and biological activity shall have a role in further converting these fertilizers into ammonium and nitrate forms.

Synthetic slow-release fertilizers are often manufactured in the shape of a spike or a pellet. The soil moisture level, temperature, and the activity of microorganisms determine the frequency at which the nutrients are released. The period during which the nutrients are released ranges from 20 days to 18 months for synthetic fertilizers [20]. Synthetic organic fertilizers are categorized into matrix-based, coated, and uncoated sub-types.

In the case of matrix-based SRFs, the active ingredient, i.e., the nutrient, is dispersed within a matrix composed of various materials such as thermoplastic polymers, gel-based compounds, rubbers, etc. The active ingredient diffuses via carrier through the facial pores of the

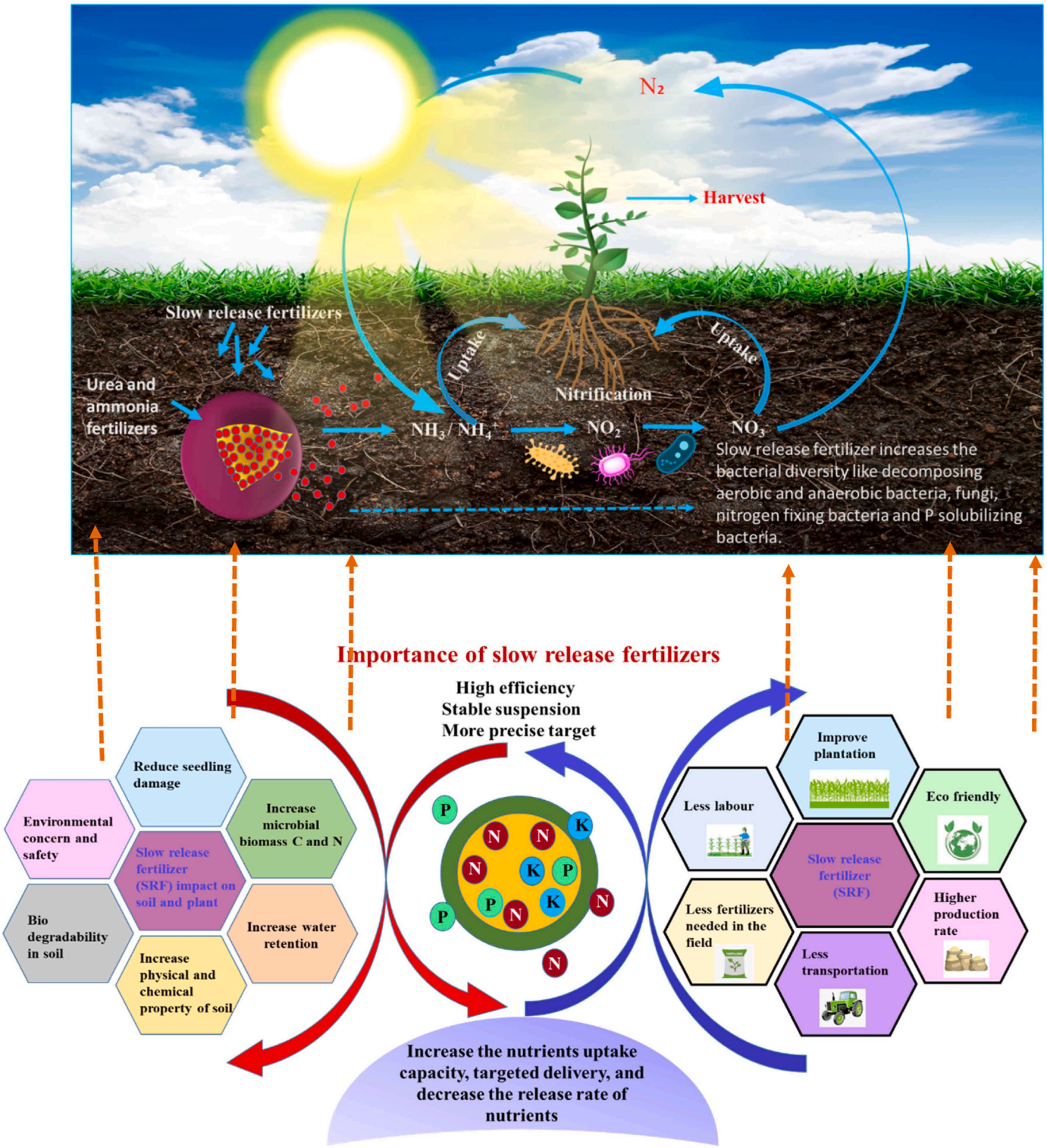
N2
Harvest
Slow release fertilizers
Urea and ammonia fertilizers
Uptake
Uptake
Nitrification
NH3/ NH4+
NO2-
NO3-
Slow release fertilizer increases the bacterial diversity like decomposing aerobic and anaerobic bacteria, fungi, nitrogen fixing bacteria and P solubilizing bacteria.
Importance of slow release fertilizers
High efficiency
Stable suspension
More precise target
Reduce seedling damage
Environmental concern and safety
Increase microbial biomass C and N
Slow release fertilizer (SRF) impact on soil and plant
Bio degradability in soil
Increase water retention
Increase physical and chemical property of soil
Improve plantation
Less labour
Eco friendly
Slow release fertilizer (SRF)
Less fertilizers needed in the field
Higher production rate
Less transportation
Increase the nutrients uptake capacity, targeted delivery, and decrease the release rate of nutrients

**Fig. 6.** Cartoon showing the mechanism of action of slow-release fertilizers in agriculture, along with benefits and ideal specifications.

matrix. The substance forming the matrix does not have any slow-release characteristics, but the morphological characteristics of the matrix help to retard the release of nutrients. In terms of shapes and morphology, there are wide varieties of matrix-based SRFs on the market, which include spikes, tablets, and briquettes, which are made up of plant nutrients and compacted using a binder. The majority of applications for these matrix-based SRF formulations are in indoor gardening. The uncoated SRFs are made up of tiny particles and are sintered with or without a binder. They are mainly used for maintaining greens and close-cut grass. Further, uncoated SRFs are homogeneous, and the composition is uniform. So, the fundamental benefit of homogenous uncoated SRFs is that, unlike coated fertilizers, their release rates are independent of the thickness of the cover. Urea-formaldehyde (UF) condensation and Isobutylidene Diurea (IBDU) are examples of some uncoated synthetic fertilizers. [19,51].

Coated SRFs provide a reasonably simple approach toward the slow

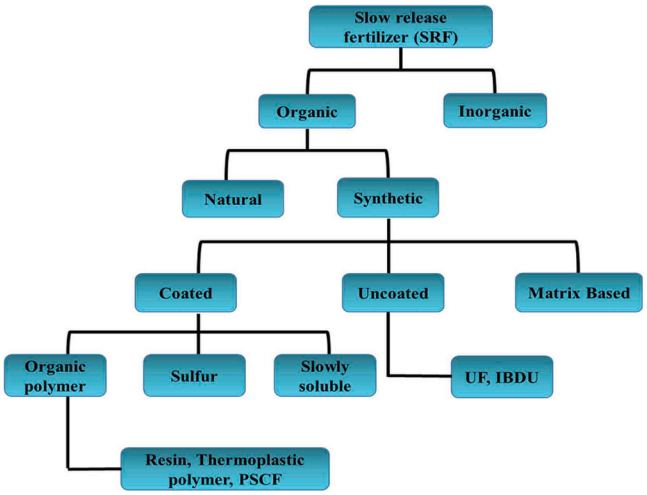


**Fig. 7.** Classification of different categories of slow-release fertilizer (adapted from [48]).

release of nutrients. They not only possess slow-release characteristics sometimes but could also have favorable release qualities under some particular circumstances [19]. Depending on the application, the type of nutrient to be released, and the targeted release rate of nutrients, the material used for the coating can be either hydrophobic or hydrophilic. Examples of coated SRFs that are generally used are resin-coated SRF, thermoplastic polymer-coated SRF, PCSF (Polymer-/sulfur-coated fertilizers), etc. The resin-coated SRFs have a cross-linked hydrophobic polymer structure for which the degradation depends on temperature. In the market, two common resin-coated materials are available: polyurethane-like coatings (e.g., Multicote, Plantacote, and Polyon) and alkyd-type resins (e.g., Osmocote). Polymer-coated fertilizers (PCFs) are the most technically advanced state-of-the-art technology for controlling nutrient release efficiency and product longevity. The nutrient release capacity of most of the PCFs is based on diffusion through their semipermeable membrane, and their release rate is controlled by varying the thickness of the coating. PCSFs are a hybrid product that utilizes a primary sulfur and a secondary polymer coating [52,53]. SCUs, or sulfur-coated urea particles, are just urea particles coated with sulfur and often with a sealant. A secondary layer of soft sealants is applied over the sulfur coating to fill any defects and maintain the integrity of the brittle sulfur shell [54]. The color of an SCU might range from brown to tan or yellow, depending on the kind of urea used and whether the sealant was applied. MagAmp, also known as magnesium ammonium phosphate, is an example of a slowly soluble synthetic fertilizer with a delayed release rate.

Compared to other slow-release fertilizers, the nitrogen level in MagAmp is relatively low, but the phosphorus amount is quite high [55].

## 4. Advantages and disadvantages of slow-release fertilizers

The SRFs are identified as fertilizers of the next generation [56,57]. The nutrient release from SRFs depends on its coating properties (i.e., composition, thickness, solubility, and porosity of the coating materials) and soil properties (soil pH and its type, moisture, microbial population, temperature, etc.). Microbial activity may break down this SRF, releasing nutrients into the soil [50]. Slow-release fertilizers help prevent nitrogen loss in the environment caused by traditional fertilizers' inefficient use. SRFs are far more advantageous than traditional fertilizers in terms of both economics and the environment. However, SRFs also have drawbacks; thus, research should focus on finding solutions. Table 1 also explains the key benefits and drawbacks of slow-release fertilizers compared to regular fertilizers.

## 5. Methods of preparation of slow-release fertilizers

There are various procedures for synthesizing slow-release fertilizers; however, the synthesis techniques fundamentally may differ for the two major types of SRFs: matrix or carrier type SRF and coating type SRF. In the subsequent subsection, we discuss the preparation methods of SRFs developed by different researchers/ commercial ventures in detail.

### 5.1. *Matrix-type slow-release fertilizer hydrogels*

Fertilizers are incorporated into the matrix of SRFs in two significant ways: in-situ and two-step processes. Both procedures use fertilizers in liquid form [58]. The matrix-type preparation technique is often used to prepare the slow-release fertilizer in hydrogel form (SRFH). Two methods are available to prepare the matrix-type SRFHs - (1) two-step and (2) in situ. SRFHs are created using the in-situ approach by encasing the liquid nutrients in the hydrogel. This approach involves mixing all the components first, including the nutrient solution, the initiator, the monomer, and the cross-linker, during the one-step polymerization process. The hydrogel thus formed is dried before its use.

In contrast, in the two-step technique, the hydrogel is synthesized and dried first, followed by soaking the dried hydrogel in a liquid nutrient solution. The dry hydrogel then begins to swell due to the ingress of the nutrient solution. The swollen hydrogel is then processed further by drying it [59,60]. Both methods have a few advantages and disadvantages. The two-step technique, which prevents side reactions from taking place while combining all the components during polymerization, offers greater control over the release rate of nutrients from SRFHs than those formed via the in-situ method [61]. The two-step technique involves many steps: synthesizing the hydrogel and drying, absorbing the liquid fertilizer by the hydrogel, and finally, drying, which makes this quite elaborate and problematic. It takes extra synthesis time since two drying procedures are involved.

In contrast, the in-situ method only requires one drying step and is relatively straightforward. However, polymerization must be controlled because impurities and unreacted elements produced during this process are difficult to remove [58]. Further, to create slow-release fertilizer in hydrogel forms, a variety of polymerization techniques have been utilized, including aqueous or solution polymerization [62], free radical polymerization [63,64], ionizing radiation [65], ultraviolet light irradiation [66], and microwave [67]. Rabat et al. made an oil palm empty fruit bunch-grafted-poly (acrylic acid-co-acrylamide) [OPEFB-g-P (AAc-co-AAm)] SRFHs by utilizing both techniques [68]. They observed that the SRFHs made by a two-step process had asymmetrical and irregular pores through which diffusion of water entered quickly into the hydrogel. However, SRFHs made through an in-situ process have fewer pores, which regulates less water diffusion inside the hydrogel, so in this study, the in-situ process is better than the two-step method for slowing down urea's release rate.

Utilizing a two-step process, [69] produced slow-release urea fertilizer using mulberry branch-g-poly [MB-g-P (AAc-co-AAm)] (acrylic acid co-acrylamide). Through polymerization, MB-g-P (AAc-co-AAm) superabsorbent hydrogel was first created. Then, the hydrogel was thoroughly combined with urea, calcium dichloride ($CaCl_2$), and sodium alginate solution to create the slow-release urea fertilizer. In another study, the two-step method was used by [70] to create a hydrogel-based slow-release fertilizer from Arabic gum. This hydrogel was created using a variety of ingredients, including acrylamide (AAm), modified Arabic gum, and ammonium persulfate (APS). After adding various components, they are thoroughly combined to form a hydrogel, which is dried. Then, it was submerged in an NPK fertilizer solution to take in the nutrients. The nutrient-rich hydrogel was finally dried to make the hydrogel fertilizer from Arabic gum.

**Table 1**
Comparison between the conventional fertilizers and slow-release fertilizers (SRFs) and their advantages and disadvantages.

| Comparison | Conventional fertilizer | Slow-release fertilizer |
|---|---|---|
| **Nutrients used for plant growth** | N, P, and K are used as plant nutrients. | Macronutrients (N, P, K) used as fertilizer |
| **Factors affecting release property** | Soil condition and water | Soil pH, temperature, and microorganisms |
| **Nutrient use efficiency** | Low | Comparatively higher than conventional fertilizers |
| **Rate of nutrient loss** | Higher nutrient loss caused by leaching, run-off, rainfall, etc. | Comparatively lower loss of nutrients due to having a semi-permeable coating layer |
| **Release pattern** | Unusual or uncontrolled manner of the release | Slow-release manner |
| **Cost and availability** | Lower cost and frequently available in the market | Moderately available in the market, the price is higher than conventional fertilizers. |
| **Solubility in water** | Highly soluble | Solubility is controlled by material resources and external factors |
| **Duration of release** | Release the nutrients in a short time | Effective duration is much higher than conventional fertilizers |
| **Size of fertilizers** | Undefined or large | Comparatively smaller than conventional fertilizers |
| **Advantages** | • Easily available<br>• Low price<br>• Easy to produce on a large scale<br>• Basic macronutrients (N, P, K) can be produced | • Increase the plant's nutrient uptake ability through the slow-release.<br>• Significantly reduce the nutrient loss, mainly nitrate, by leaching and ammonia through volatilization.<br>• Reduces the risk of environmental pollution.<br>• SRFs are economically valuable, utilize less labor and energy, are time-saving, and easy to use method.<br>• SRFs do not allow for any nitrogen deficiency symptoms, usually caused by conventional fertilizers.<br>• SRFs decrease toxicity to plants caused by high ionic concentration resulting from the quick dissolution of urea; through this, agronomic safety is improved.<br>• Using slow-release fertilizer on trees and crops planted on slopes is beneficial because the nutrients applied in the slops cannot be washed away after watering or due to rainfall. |
| **Disadvantages** | • Increases the plant toxicity and leads to groundwater pollution<br>• Over-fertilization due to that high labor is needed<br>• It is highly volatile and reduces soil fertility | • The cost of manufacturing slow-release fertilizer is higher than conventional fertilizers, limiting their general use in agriculture.<br>• Soil acidity may rise due to the use of coated fertilizers.<br>• Farmers have less knowledge about the application methods of SRFs and less technical support from manufacturers and distributors.<br>• Polymer-coated or encapsulated slow-release fertilizers leave the toxic residues of synthetic material in the soil.<br>• The duration of nutrient release cannot be controlled due to microbial activity. |

### *5.2. Coated-type slow-release fertilizer hydrogels*

Coating fertilizers is another method for regulating the rate at which nutrients are released. Urea [71], di-ammonium phosphate fertilizers (DAP) [72], and nitrogen, phosphorus, and potassium (NPK) are utilized as sources of nutrients in the synthesis of coated fertilizer [73]. These solid fertilizers can be rendered slowly soluble with various coatings, including organic, inorganic, and superabsorbent polymers, thus making it possible to have different varieties. The hydrophilicity or hydrophobicity and porosity of the coating material are the key determinants of the release rate of the coated SRFs [74]. Materials of choice for the coating may vary widely, such as polystyrene [75], polysulfone [74], acrylonitrile-butadiene-styrene polymer, and polypropylene [1,76]; they all have been used to create a coating of SRFs. These polymers constitute the outer surface and help to reduce the diffusion of water into fertilizer and prevent consequent dissolution, which leads to the phenomenon of controlled release of nutrients. The development of multilayer coating also decreases the nutrient release rate by making a thick, compact, dense structure with fewer pores [74,77]. One drawback of the polymer-coated SRF is the polymeric residue that remains after the nutrient is consumed; it has been reported that such residue can be as high as 50 kg/(ha. year) [20]. Thus, for large-scale use, the coating material must be biodegradable. The materials used for the coatings on the SRFs have to decompose naturally without causing any damage to the surrounding ecosystem [78]. In a significant number of investigations, coating techniques using natural polymers such as chitosan [71], starch [79], or polyvinyl alcohol (PVA) [80] were used to coat the solid fertilizer.

Chitosan and polyvinyl alcohol combined with urea were the basis for the development of SRF in this study [81]. A chitosan solution was prepared by adding chitosan to a mixture of acetic acid and distilled water. Polyvinyl alcohol was added to this chitosan solution to create a transparent solution. The mixture was then chilled until it reached room temperature. The chitosan/polyvinyl alcohol solution was then supplemented with urea. Later, glutaraldehyde was gradually added to create a hydrogel that was dried in an oven set to 50 °C. In a study by Zhao et al., Castor oil (CO) was used to create a novel hybrid polymer using a one-pot method [82]. Urea prills were mixed with an appropriate quantity of castor oil-based polyurethane to form a coat on the prills, and the coating process was repeated until 5 % coating comprising polymer-coated urea (PCU) was achieved. This method did not create any byproducts, nor did it require any solvents. In another study, the urea granules were coated using the rotating pan method by [83] utilizing gypsum, dolomitic limestone, sulfur, and palm polyols. The coating components and urea granules were mixed in a rotating pan before introducing water. This reaction was carried out constantly until a homogenous coating formed on the urea granules and all the ingredients were thoroughly combined. The coated urea granules were then dried in the air. The results showed that a protective layer around urea granules slowed down the fertilizer's release rate and reduced the coated fertilizer's crushing strength. Additional examples of preparation processes for making slow-release fertilizers are included in Table 2.

## 6. Nutrient release mechanism of slow-release fertilizers

Inorganic SRFs generally include low-solubility metal-based ammonium phosphate compounds (generally known as struvite) or partially acidulated phosphate rock (PAPR). They need to be dissolved so that the ammonium and phosphate ions can be released into the soil. However, due to the low solubility, the dissolution kinetics of struvite crystals are pretty slow; it mainly depends on the pH of the soil or, more specifically, the moisture in the root zones of the plants. Generally, the soil's pH does not vary significantly and remains within the range of 5.5–7.5 [95]. Slightly acidic soil may promote faster dissolution; however, struvite is mostly stable in the pH range of 7.7–10.6. According to the Nernst--Brunner stagnant film theory, a solid phase dissolves in a liquid phase by transferring a solute from the surface of the solid phase into the neighboring solvent (liquid) phase. Thus, the concentration of solute inside a stagnant liquid film of a certain thickness immediately surrounding the solid surface may be assumed to reach the particle solubility or

saturation concentration ($C_s$) and at the outside of the diffusion layer may be assumed to be at a bulk concentration ($C_b$). The dissolution kinetics of Struvite was reported to be according to the following Eq. 1 [96].

$$\ln(C_s - C_b) = \ln C_s - k_L a.t \quad (1)$$

Where $k_L$ is the mass transfer coefficient, $a$ is the specific surface area (surface area per g of crystal), and $t$ is the dissolution time. Ariyanto et al. (2017) reported that dissolution is a diffusion rate-controlled process beyond a temperature of 11°C, and the dissolution rate is positively correlated with the temperature. As per Nernst-Burrner's theory, the dissolution rate is proportional to the surface area of crystals; in other words, the specific surface area of the struvite particles should influence the dissolution kinetics. However, Ariyanto et al. also reported that due to the high specific surface area available with small sizes of struvite crystals, practically the dissolution kinetics were unaffected by the size of the crystals [96].

The industry has different opinions on the difference between controlled-release fertilizers (CRFs) and slow-release fertilizers (SRFs). Arguably, the mechanism of CRFs is different from that of SRFs. The American Association of Plant Food Control Officials (AAPFCO) does not formally distinguish between CRFs and SRFs, even though an SRF covered by a coating is also referred to as a CRF [97]. This coating material may consist of sulfur, polymers, and resins or can combine sulfur and polymers [98]. In CRFs, a coated fertilizer, the core of fertilizer is encapsulated with a semipermeable coating material; the slow release of the nutrients from the fertilizers is controlled by this layer while regulating the flow of water into the core simultaneously. CRF's rate of nutrient release is influenced by the coating's composition, thickness, diffusion characteristics, soil moisture, and temperature. However, on the other hand, SRF's nutrient release rate depends on microbial activity, soil moisture, and temperature [99].

Hydrophobic materials like polymers are often used to prepare controlled-release fertilizers because of their relative independence to the soil characteristics and environmental factors, making it possible to control the release characteristics reasonably. Ideally, the pattern of release of fertilizers from the CRFs should be sigmoidal [100], which resembles the pattern of nutrient uptake by plants. Such a release pattern helps reduce the environmental and health threats related to the release of fertilizers into surface water bodies through agricultural run-offs. Although it is argued that several split applications [101] of N-fertilizer during plant growth may be more effective than a slow--release fertilizer, the impediments are the intensity of labor requirement, dependence on weather and field conditions, often resulting in extra applications and labor-inflexibility. Therefore, in practice, effective synchronization between supply and uptake can be achieved by the use of slow- or controlled-release fertilizers, where in order to find the appropriate fertilizer, it is necessary to predict the nutrient release rates.

While the sigmoidal release pattern suggests that the release pattern would be anything but following a simple Fickian diffusion mechanism, the early models were developed based on the assumption that the release of nutrients across a membrane or a diffusible barrier is a simple process of diffusion and ignored any role of water uptake or other mechanisms which make this process far more complex than simple Fickian diffusion [102]. There were efforts to model the release of the nutrients by introducing several other parameters, such as a time--dependent diffusion coefficient, a failure or rupture phenomenon depending upon the pressure built inside the granules, or applying Fick's law in spherical coordinates. They successfully predicted the linear and decaying release process but could not account for the lag period before the linear release of the nutrient begins [102,103].

Shaviv put forward a detailed conceptual model of the nutrients released by a coated fertilizer [104]. The model recognized three different stages of the nutrient release, which are mentioned below:

**Table 2**
Preparation methods of slow-release fertilizers.

| Type of fertilizer | Classification | Preparation method | Reference |
|---|---|---|---|
| Natural rubber-g poly (acrylic acid) NR-g-Poly (AAc) outer coated urea/ dipotassium phosphate/ attapulgite | Coated | By the use of a pan granulator, urea, attapulgite, and dipotassium phosphate were granulated. In carbon tetrachloride, natural rubber was immersed and sprayed on the outer surface of the fertilizer to make the first coating layer. NR-g-Poly(AAc) was made by radical solution, NR-g-Poly (AAc) was crushed and attached to the outer surface of natural rubber as a second coating layer. | [84] |
| Phosphate bound-carboxymethyl starch-graft-polyacrylamide (PCMS-g-PAM) | Matrix or carrier; In -situ | Phosphorylated carboxymethyl starch (P-CMS) was dissolved in water at 50 °C with continuous stirring in a nitrogen environment. Then, in this solution, acrylamide (AM) and N, N′-methylene bis acrylamide (MBA) were added, respectively. After that, potassium persulfate was added, and it helped to initiate the grafting reaction. The mixture of material was dried in a vacuum oven. | [85] |
| Lignin-based slow-release fertilizer | Coated | The urea, formaldehyde, and lignin mixture is added into distilled water at 80 °C with continuous stirring at 80 rpm for 120 minutes. Then, dipotassium hydrogen phosphate trihydrate and sodium hydroxide solutions were added. After that, these products were dried at 50 °C in the oven. | [86] |
| Millet straw phosphate-graft- acrylic acid/ polyvinyl alcohol-ammonium polyphosphate (MSP-g-AA/PVA-APP) | Matrix or carrier; Two-step | Cellulose was extracted from millet straw. For millet straw phosphate (MSP) preparation, an equal amount of sodium dihydrogen phosphate and cellulose were added at 25°C, continued stirring for one hour, and then dried in an oven at 130°C. After that, MSP was put and dispersed at 60 °C in a three-necked flask. Further, potassium persulfate and ammonium persulfate were added. | [87] |

(continued on next page)

**Table 2** (*continued*)

| Type of fertilizer | Classification | Preparation method | Reference |
|---|---|---|---|
| | | Then, urea and a solution of acrylic acid were added at 80°C. After 15 min, ammonium polyphosphate and polyvinyl alcohol were added, and methylene bis acrylamide was mixed as a cross-linker and kept for three hours of stirring. Finally, the products were dried at 70°C in the oven. | |
| Cellulose containing diene units-graft-polymer(acrylic acid)/Urea (CCDEUs-g-poly(AA)/urea) | Matrix or carrier; Two-step | Cellulose containing diene units (7.9–29.1 wt%) and distilled water were added at 90°C and stirred for 10 min. Then, acrylic acid, ammonium persulfate, N, N′-Methylene bis acrylamide, and urea were added to the mixture, respectively. This reaction mixture was stirred at 70 °C, and the semi-solid product was made. The completion of the polymer reaction takes 90 min. Then, a polymer material was formed. This polymer was dehydrated using a methanol solution and dried at 65 °C in the oven. Next, it was immersed in distilled water. Finally, the soaked polymer was filtered and dried at 65 °C in the oven again. | [88] |
| Multifunctional eco-friendly fertilizer developed from keratin-based superabsorbent | Coated | Lignin powder and urea granules were slowly added to the rotating pan. Then, the cores of fertilizer were made through water atomization and dried at 40°C. The inner coating surface was prepared through solution spray (5%, w/v) on the core surface of the fertilizer. Next, the keratin-based superabsorbent powder is utilized as the outermost layer of coating. In the end, the product was dried in the oven at the same temperature. Finally, the double-coated multifunctional eco-friendly fertilizer was obtained. | [89] |
| Banana peel cellulose-polymer-acetic acid/ vinyl alcohol/ Layered double hydroxides (BPC-g-Poly-AA/VA/LDH) | Matrix orcarrier; In situ | Cellulose from banana peel was added to water and stirred at 50°C for 10 min. Layered double hydroxides, ammonium dihydrogen phosphate, and urea were added in stirring conditions. In inert conditions, AAc, APS, N, N′-Methylene bis-acrylamide were added for the polymerization reaction, and the obtained product was grinded and used for further use. | [90] |
| Polyester-lignite composites (SRFs; Poly3 and Poly5) | Coated | 100 g of granular urea was combined with 2 g of polyester resin in a rotating drum coater (30 rpm), and 3 g of fine lignite powder was added on top of the mixture. The mixture was allowed to dry on a flat tray at room temperature for 30 minutes. This SRF is known as Poly3 and was coated similarly three times with a polyester and lignite combination. Another 100 g of urea was used in the procedure, but a polyester-lignite composite was applied five times this time, creating Poly5. | [91] |
| CSt-g-PAA/NR/PVA semi-IPN (CSB) multicomponent hydrogels | Coated | Initially, a mixture of CSt powder and 40% NaOH as a hydrogen-bond breaking agent was combined in a round-bottom flask and subsequently subjected to heat for the purpose of gelatinization. Subsequently, APS was introduced to commence the reaction. The AA monomer and cross-linking agent were utilized following an intense magnetic stirring process to generate the cross-linked CSt-g-PAA solutions. Meanwhile, Polyvinyl alcohol (PVA) was solubilized in deionized water and subsequently blended with Natural Rubber (NR) latex and Emulvin under ambient conditions. Following this, the solution, including a blend of PVA and NR, was introduced into the hydrogel solutions | [92] |

(*continued on next page*)

**Table 2** (*continued*)

| Type of fertilizer | Classification | Preparation method | Reference |
|---|---|---|---|
| | | of crosslinked CSt-g-PAA and subjected to heating to attain the semi-IPN hydrogel solution. | |
| Monolithic urea-embedded starch-based hydrogels through grafting acrylamide (AM) | In-situ radiation-synthesis | After being subjected to Cobalt-60 γ-rays during the homogenization of a starch and AM combination, the hydrogels were immediately dried and crushed into granules (100-200 μm). | [93] |
| Coal fly ash to zeolite A (ZA) | In-situ impregnation of urea | A solution was prepared by mixing ZA or CL with deionized water. Subsequently, varying ratios of urea and zeolite were introduced to the suspension, specifically at ratios of 1:1, 1:2, 1:5, and 1:10. The suspension underwent stirring for a duration of 2 hours and was subsequently subjected to drying at a temperature of $55^0$C for a period of 24 hours until complete evaporation of water was achieved. | [94] |

1. Lag period: The vapor pressure gradient between the solid core of the fertilizer granule and the surrounding results in a driving force that helps the water vapor cross the membrane coating to occupy the voids existing within the core and the coating. The time required to fill the void up to a threshold water volume within the granule may be termed the lag period, up to which there is little or no release of the fertilizer
2. After a threshold volume of saturated solution is reached within the granule, the nutrient is constantly released from the fertilizer granule. The fertilizer transport outside the granule is driven by a constant concentration gradient between the saturated solution inside and comparatively negligible concentration in the external solution. The saturation concentration is maintained within the granule while in equilibrium with the undissolved solid fertilizer. As long as the saturation concentration is maintained, the release rate of nutrients from the fertilizer remains constant.
3. After all the fertilizer gets dissolved, the internal concentration gradually drops because of the non-availability of undissolved fertilizer and the continuous ingress of water within the core. When this happens, the release rate of nutrients from the fertilizer to the external solution also decreases. It is known as the decay phase.

A mathematical model based on the above conceptual process can be explained by Eq. 2 [104],

$$g(r,I,t) = \begin{Bmatrix} 0 \quad t < t' \\ \frac{P_s A C_{sat}}{IQ}(t-t') = \frac{3P_s C_{sat}}{rI}(t-t'), \quad t' \le t < t^* \\ \left(1 - \frac{C_{sat}}{\rho_s}\right)\exp\left[-\frac{3P_s}{rI}(t-t^*)\right], \quad t \ge t^* \end{Bmatrix} \tag{2}$$

Where r is the radius of the granule, I is the coating thickness, g is the fractional release of nutrients at time t, $P_s$ stands for solute permeability, A is the surface area of the granules (considering a sphere), $C_{sat}$ is the saturation concentration of the solute or nutrient, Q is the total mass of the fertilizer stored in the granule, $t'$is the lag period, and $t^*$ is the duration of linear release.

Rather than the slow release, some granules would go for bursting or rupture, mainly due to their internal architecture and coating characteristics. Zaidel (1996) proposed the following expression (Eq. 3) for estimating the time of burst or rupture, $t_b$:

$$t_b \cong \frac{rIY}{P_h \Delta \pi M} \tag{3}$$

Where Y is the yield stress of the coating, $P_h$ is the water permeability of the membrane or the coating, $\Delta\pi$ is the osmotic pressure differential across the membrane, and M is Young's modulus of elasticity of the coating [105].

The mathematical models described above are based on a single granule. However, in practice, where there is a plurality of such granules of different sizes and membrane coating thicknesses, a new model with statistical correction would be needed. Zaidel (1996) proposed a variation of this model for a large population of coated spherical granules, which differ in granule radius, r, and coating thickness, I. The general findings that can be summarized are: (1) membranes with lower water permeability should have a more extended lag period. Lower solute permeability in the membranes would reduce the rate of release of the nutrients, (2) a larger average size of the granules and thicker membrane coating would result in a more extended lag period, which means that granules with a larger range of sizes would result in a short lag period but longer release time; and, (3) Diffusion mechanism is less sensitive to the changes in the structural properties of the fertilizers than the failure mechanism.

## 7. Factors affecting the performance of slow-release fertilizer

Environmental conditions in the soil, including temperature, moisture, pH, soil texture, and microbial population, all have a role in the nutrient release from SRFs. The following is a discussion of the factors that affect slow-release fertilizers.

Temperature - According to various research studies, temperature is a significant factor influencing SRFs' release of their nutrient content. The microbial activity in the soil influencing the rate of nitrogen release from SRFs increases when soil temperature rises, leading to an increase in the rate of nutrient release [106,107] - an increase in temperature results in the elevation of vapor pressure inside the soil. Water vapor formed within the soil diffuses into coated SRFs during the initial phase of the release of nutrients from SRFs. Once the water vapor condenses, the hydrostatic pressure within the SRF rises. As a result of the strong hydrostatic pressure within the SRF, the release of the nutrients is accelerated, causing a mass outflow of the nutrient solution. According to another research study, the researcher argues that due to high osmotic pressure within, the SRF swells, causing the pores of the SRFs to grow more prominent due to the rise of temperature, leading to a more significant release rate. Additionally, it was found that a $15^0$ C rise in temperature caused the release rate to almost double [108]. According to [109], it is needless to say that the diffusion of the nutrient ions is faster at $37^0$ C than it is at $25^0$ C.

Soil pH - It has been shown that the pH of the soil does not directly impact SRFs. The pH of the soil affects the microbial population and its activity. Enzymes produced by bacteria are essential for degrading the nutrients released by biodegradable SRFs, and each enzyme has a unique pH requirement. Enzymes cannot function effectively when the pH is not conducive. For some types of fertilizers, such as sulfur-coated urea-based fertilizers, a low soil pH creates circumstances conducive to gradually releasing nutrients [110].

Soil moisture - The high soil moisture content accelerates the

mineralization of SRFs. The reason behind such an assertion is that increasing moisture content in the soil enhances the activity of the microorganisms responsible for the release of nutrients from SRFs; thus, the availability of nutrients in the soil is higher as a consequence [111].

Soil Texture – The relative proportion of soil sand, silt, and clay particles governs soil texture. Soil texture alone cannot affect the nutrient release rate. However, soil texture influences soil characteristics like moisture-holding capacity and temperature, which affect the nutrient release rate of material [112,113].

Coating Thickness - It is evident that the thickness of the coating SRFs plays a significant role in controlling the nutrient release rate [114]. The membrane or coating surrounding the core of the SRF is the barrier across which the nutrients diffuse under a concentration gradient, and according to Fick's law, the diffusion rate across the barrier is inversely proportional to the thickness of the membrane. Thus, the increase in the coating thickness can extend the lag period of nutrient release, which can also slow down the release rate of nutrients [20,115]. According to [116], when a hydrophilic polymer-coated fertilizer is submerged in water, it expands due to water moving through the polymer coating during the imbibement process. The nutrients in the core of SRFs are promptly dissolved by water as it travels through the dynamic gaps between the polymer's macromolecules. In addition, inside the coated shell of SRFs, hydrostatic pressure is generated once the water condenses. The polymer coating of SRFs begins to break down under hydrostatic pressure, and nutrients flow out of the micropores that have formed on the coated surface [117].

Microbial activity- The primary agent responsible for the release of nutrients from biodegradable coated material of SRFs is the microbial population in the soil, which forms colonies on the coating surface of the SRFs and then secretes various kinds of hydrolysis enzymes that break down the biodegradable coating surface of the SRFs and release the nutrients. Temperature, pH, moisture, and other environmental elements in soil, as well as microbial population and activity, all have a role [118,119]. The soil's high temperature and high moisture content are ideal for microbial activity and development, which speeds up the metabolization of coated surfaces [120]. Table 3 also discusses the breakdown of slow-release fertilizer by different microorganisms and their enzymes [118].

## 8. Material resources

### 8.1. Organic form of slow-release fertilizers

Research into sustainable and biodegradable materials used in this sector has increased to prevent environmental pollution and the buildup of non-biodegradable material on Earth [122]. Therefore, biodegradable polymeric materials made from natural sources may reduce the buildup of harmful waste, and it is often more affordable to create than synthetic materials [20]. Biological polymers like cellulose, chitin, lignin, starch, and other polysaccharides seem to be an alternative to synthetic fertilizers and could help organic waste recycling and the circular economy [123]. The release behavior of nitrogen for plant development was examined by using a double-coated slow-release fertilizer [79]. Ethylcellulose (EC) was used to create a slow-release fertilizer, while starch-SAP (starch-based superabsorbent polymer) was used to create the outer coating. The starch-SAPs from three plant sources, potato, maize, and cassava, were synthesized using the twin-roll mixer technique. Researchers discovered that the urea particles coated with starch-SAP and EC had an excellent slow-release capability compared to those coated with and without ethyl cellulose (EC). Particularly, material prepared with potato starch-SAP had a superior rate of constant nutritional release than material made with other botanical sources (maize, cassava). Fig. 8 **(A)** represents the rate at which various botanical sources' fertilizer particles, both coated and uncoated, release nutrients into the soil at room temperature, **(B)** describes the relationship between the properties of starch-SAP and the slow-release behavior of double-coated fertilizer in a schematic manner. This study has shown that starch-SAP from different plant sources can be used to make double-layer coated fertilizer that makes plant nutrients work better.

The lignocellulosic biomass extruded composite material for the gradual release of nutrients was created by [124]. On a lab scale, many kinds of coated slow-release fertilizers are made utilizing urea/HAP powder as the base fertilizer. A covering made of wood-derived materials such as SCB (sugarcane bagasse), cellulose, and lignin encapsulated this basic fertilizer. According to this research, impregnation of urea with HAP causes the amine functional group of urea to bind strongly with the carbonyl group on the surface of HAP, functionalizing fertilizer. The urea/HAP that was not encapsulated had a great slow-release pattern, but it was not as efficient as coated fertilizer made of wood--derived components (SCB, cellulose, lignin). The urea-impregnated HAP encapsulated by lignocellulosic biomass composites made of SCB, cellulose, and lignin revealed a delayed and persistent nutrient release over 60 days compared to an uncoated material, according to the water immersion experiment. Compared to other coated materials, the urea-impregnated HAP enclosed in lignin exhibits superior performance.

Biochar is a carbon-based material derived from the thermal breakdown of plant and animal biomass under a limited oxygen supply. Applying biochar improved root colonization and mycorrhizal fungus spore germination through improved soil properties and nutrient availability[11,125,126]. Recently, researchers discovered that adding biochar can boost soil water retention capacity [127]. Soils modified with biochar might hold more water from rainfall, thereby increasing agricultural output in non-irrigated dryland zones [128]. Biochar's residence time in the soil is often hundreds to thousands of years, allowing for longer-term changes in the community of microbes [11]. Biochar is often effective at promoting microbial growth, enhancing nutrient accessibility, and influencing crop yield [126]. Adding biochar to soil can improve soil pH, reduce greenhouse gas emissions, reduce nutrient losses, and reduce fertilizer demand. It can also increase ammonia and nitrate retention, water and nutrient retention in light--textured soils, increase cation exchange capacity (CEC) in soils with low organic matter content, and improve soil physical properties like aeration and porosity [129]. A hydrogel-biochar composite based on pine resin was utilized as a carrier for controlled release in a study by S. K.

**Table 3**
Microorganisms and their enzymes responsible for degrading some biodegradable coating materials of Slow-release fertilizer [118].

| Polymer coating urea | Characteristics | Biodegradability | Microorganisms and their enzymes responsible for the biodegradability |
|---|---|---|---|
| Polyurethane | Synthetic polymer | Partially | *Petalotiopsis micropora* secretes "Polyurethanase" enzyme |
| Chitosan | Polysaccharides derived from chitin, nontoxic | completely | Bacteria producing "chitosanases": *Streptomyces* spp. And *Kitasatospora* spp |
| Alginate | Natural polymer andnontoxic | completely | *Asteromyces cruciatus* and *Dendryphiella salina*"Alginate hydrolase" enzyme. |
| Starch | Natural polymer is easily modified and nontoxic | completely | Amylases, amyloglucosidases, and transglucosidases [121] |
| Lignin | Made from plantderivatives, low cost | completely | *Actinomycetes*, α-*Proteobacteria*, γ-*Proteobacteria* produce the "Laccase" enzyme. |

Das et al. [130]. The N-P-K fertilizer was synthesized using the graft--polymerization technique, where pine resin was employed as the polymer matrix, persulphate potassium as the initiator, MBA as the crosslinking agent, and acrylamide as the monomers. Different proportions of initiator, cross-linkers, and monomer were employed to produce various compositions of controlled-release fertilizers (CRF) based on biochar-hydrogel. The biochar, loaded with N-P-K nutrients, was chemically linked with hydrogels through polymerization. The composite exhibited the capacity to increase water retention by 57.20–67.61 %. After a period of incubation lasting around 288 days, the proportion of N-P-K nutrition released in distilled water was determined to be less than 85 %. The N-P-K nutrient release rates of LCBH-SRF exhibited positive results in soil, with a greater rate of nitrogen release than phosphorus and potassium. During 45 days, the LCBH-$SRF_1$ released nitrogen at a rate of 62.57 %, phosphorus at a rate of 42.56 %, and potassium at a rate of 35.46 %. The results revealed that the quantity of nutrients released varied between 2.87 % and 7.52 % on day 3 and did not exceed 34.49–90.23 % on the 45th day. The results indicated that the controlled release properties of LCBH-SRF, as determined in this study, conformed to the methodology set by the Committee of European Normalization (CEN) for slow-release fertilizers. The LCBH-SRF exhibited a release of N-P-K in soil below 90 %. The controlled-release fertilizer that was used in this study followed the Korsmeyer-Peppas model. The observed behavior displayed notable variations from the usual diffusive characteristics that are often observed in porous media. Furthermore, this method has the capacity to enhance the use of organic materials like pine resin in the production of hydrogels, leading to a substantial decrease in research and development costs [130].

The study by S. k. Das et al., investigated the effects of a slow-release NPK fertilizer derived from biochar. The study examined its impact on soil health, leaching behavior, crop production, and nutrient release patterns utilizing nutrient impregnation technology. The biochar was subjected to a temperature of 600°C and immersed in a nutrient solution for 72 hours. Subsequently, it was mixed with a starch-PVA binder in a ratio of 1:5 to achieve a homogeneous coating. The experiment utilized four different forms of biochar for the preparation process: MSB (maize stalk biochar), BGB (black gram biochar), PNB (pine needle biochar), and LCB (Lantana camara biochar). Furthermore, the pine needle biochar (PNB) showed the most significant ability to retain and absorb nutrients among the four different kinds of biochar. In contrast, the maize stalk biochar (MSB) displayed the lowest capability. The SRF exhibited an ability to release nutrients gradually. The leaching procedure utilized 160 mL of water, comparable to 462.18 mm of rainfall. Approximately 47.60–58.27 % of nitrate ions ( $NO_3^-$), 47.84–65.40 % of ammonium ions ($NH_4^+$),), and 58.05–59.07 % of potassium oxide ($K_2O$) were successfully extracted from a column depth ranging from 40 to 50 cm during this process. This suggests that the SRF efficiently retains the nutrients in the upper layer of soil and restricts the potential for leaching. Biochar decreased nitrogen (N) and potassium (K) downward movement rate in a compacted soil column. Using biochar-based slow-release fertilizer (SRF) resulted in a significant improvement in crop production and yield attributes, above the effects of traditional fertilization methods. Hence, the biochar-derived slow-release NPK fertilizer could be employed to maximize the advantages of incorporating NPK into sandy soil while mitigating its adverse environmental impacts [131].

In another study by S. K. Das et al. [132], a secondary and micronutrient-enriched nano-fertilizer was developed using four different types of biochar (MSB, BGB, PNB, and LCB) as a carrier. The nano--fertilizer was created through impregnation and then subjected to physicochemical characterization. Additionally, the study compared the cumulative concentrations of nutrient release behavior of the developed nano-fertilizer with that of conventional chemical fertilizer. The nano-fertilizer that was created showed a remarkable ability to absorb water, ranging from 32.46 % to 45.76 %. The study on nutrient release patterns showed that after 90 days, the concentration of $Ca^{+2}$ released ranged from 87.4 % to 90.7 %, $Mg^{+2}$ ranged from 81.8 % to 85.3 %, $Na^{+}$ ranged from 96.2 % to 99.1 %, $Fe^{+2}$ ranged from 2.8 % to 5.2 %, and $Zn^{+2}$ ranged from 0.5 % to 1.6 %. Following the pine needle biochar (PNB), the Lantana camara biochar (LCB), black gram biochar (BGB), and maize stalk biochar (MSB) demonstrated slower release of these nutrients. However, the biochar from Lantana camara has shown a significant ability to retain and sorbing $Zn^{+2}$ nutrients, above the biochars derived from pine needles, black gram, and maize stalks. Therefore, the different feedstock types influenced the nutrient release pattern of the secondary and micronutrient from the designed nano-fertilizer. Using biochar-based nano-fertilizers can reduce nutrient leaching, improve water retention, and consequently enhance plant nutrient and water utilization efficiencies [132].

The study by S. Fertahi et al. utilized lignin polymers derived from various plant biomass as coating materials for P fertilizers, aiming to create slow-release fertilizers. Three types of lignocellulosic biomass, specifically olive pomace (OP), and barley straw (BS), wood shavings (WS), were utilized as feedstock for the extraction of lignin polymers; they were used as a covering for triple super phosphate (TSP) fertilizer. A study found that lignin-coated fertilizers, specifically TSP@L-OP, exhibited a distinct slow phosphorus release compared to TSP@L-WS, TSP@L-BS, and pristine TSP. This confirms that the botanical origin and chemical structures of lignin have a significant influence on the properties of the coating material. After 3 days, the uncoated TSP showed a complete release of 100 % P. In contrast, the released amount for

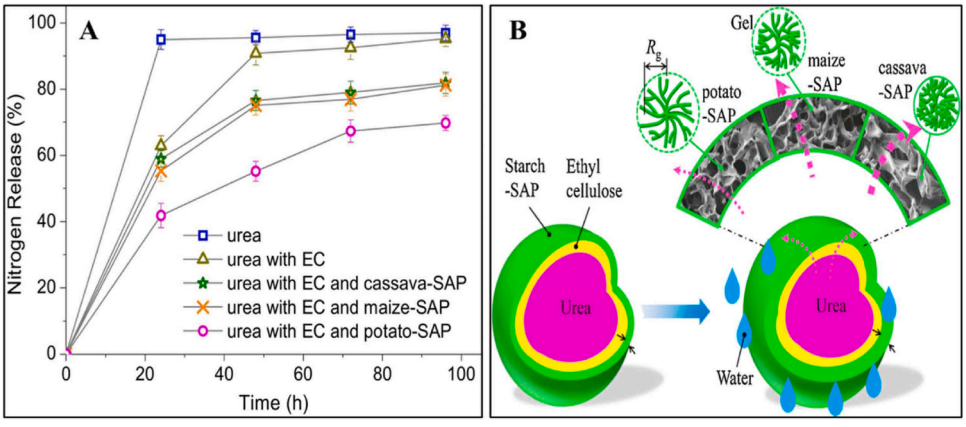


**Fig. 8. (A)** The nutrient release rate of various coated and uncoated materials, **(B)** The release behavior and characterization of Starch-SAP (reused from [79] with permission).

TSP@L-OP is 16.9 % and 33.4 % for TSP@L-BS. The study also determined the influence of these fertilizers with a coating on the absorption of nutrients and wheat growth. The results indicated a significant enhancement in the biomass of wheat shoots, providing further evidence of the beneficial effects of slow-release phosphorus fertilizers on plant growth [133].

The study done by C. Banik et al., investigated the effectiveness of SRF pellets containing varying mass ratios of biochar and urea, together with traditional N-fertilizers, in enhancing the N usage efficiency of maize (Zea mays L.). Using biochar-based slow-release fertilizers (SRF) resulted in a considerable reduction in nitrate leaching loss for both types of soil compared to conventional fertilizers. The SRF formulations resulted in an increase in maize shoot biomass (ranging from 1 % to 34 %) and root biomass (ranging from 0 % to 23 %), as well as an improvement in N-recovery efficiency (ranging from 17 % to 50 %) and soil potential mineralizable-N compared to urea and S-coated urea. The findings also suggest that the BCN ratio in the SRF formulation can be utilized to control the time of nitrogen release and the uptake of nitrogen by plants. The findings of the greenhouse study indicate that biochar-based SRFs show promise in terms of both agricultural and environmental advantages [134].

A new and biodegradable composite hydrogel was synthesized by chemical cross-linking employing gelatin (Gel), chitosan (CS), and polylactic acid (PLA) as essential ingredients by W. Yuan [135]. The solution immersion approach was used to load urea, a nitrogen source, into this novel biodegradable hydrogel. The results indicate the amount of urea may be regulated in an aqueous urea solution with varying concentrations. Initially, the release rate of urea was relatively rapid, followed by a progressive decrease in the release rate and eventually reaching a stable rate. The release kinetics in the aqueous phase conformed to the Ritger-Peppas model. The gelatin/chitosan/PLAurea (GCPU) composite hydrogel exhibited a cumulative nutritional release rate of 20 %, 70 %, and 86 % during 10 minutes, 180 minutes, and 900 minutes, respectively. Compared to pure urea, The diffusion time of urea in GCPU was increased by a factor of 1350. Furthermore, the GCPU has excellent water absorption and water retention characteristics, with an average water content that may reach up to 4448 %. All the findings in this study demonstrated that the GCPU hydrogel had excellent water absorption and retention capabilities and slow-release features for nitrogen.

Priya et al. investigated that the swelling studies showed that because of its porous structure and the presence of many polar groups, the thermally stable urea-loaded CNF/CMC hydrogel (UCNF) had a significant water absorption capacity of 147 g/g in distilled water. It discharged the moisture it had accumulated over the course of two weeks when exposed to a dry environment. The rate of urea release was quite modest; it took around 30 days for all of the urea in UCNF to be released. The results showed that urea diffusion from the material had non-Fickian behavior and aligned closely with the pseudo-second-order kinetics model. The hydrogel exhibited exceptional biodegradability, with over 80 % of its weight being removed by biodegradation by soil microorganisms during a period of 3 months. According to the plant study, adding UCNF to the soil greatly enhanced the plant's ability to germinate and grow. In addition, the plants treated with hydrogel containing urea showed better growth than the samples of pure urea and control plants. The findings of the study demonstrated the effective and continuous transportation of water and fertilizer at a regulated rate by crosslinked and functionalized cellulose nanofiber [136].

Assimi et al. [137], used the chitosan-MMT composite as a coating material for DAP (diammonium phosphate). Chitosan-MMT was utilized as the inner coating to the entrapped granular material. At the same time, PW (paraffin wax) was employed as the outside coating of DAP and served as the initial water barrier. A comparative study between coated and uncoated DAP findings showed that coated material significantly delays the ability to release phosphorus compared to uncoated DAP. Using paraffin wax (PW) as a coating material improved the hydrophobicity of the substance to provide slow-release properties. Additionally, the results of the biodegradation test and the composite material in the soil demonstrated that the coating material acts as a carbon source for the microbial population after fertilization, demonstrating its biodegradability [137].

The starch acetate/glycerol/polyvinyl alcohol biocomposites for the gradual and sustained release of nutrients were created by A. Sofyane [72]. Acetate/glycerol/polyvinyl alcohol materials were used as an outer hydrophobic coating to control the nutrient release of phosphorous (P) and nitrogen (N) from DAP (diammonium phosphate) at different proportions. The results showed that the starch acetate acted as a physical hydrophobic barrier delaying the nutrient release rate from DAP granules. Uncoated DAP completely solubilized the nutrients in water within 80 minutes. Still, coated DAP with single and double layers reached the equilibrium state to release the profile at 200 and 270 minutes, respectively. A slow-release fertilizer based on lignin and poly (vinyl acetate) (PVAc) bio blend was created by Santos [138]. The PVAc and lignin combined with urea enhanced the nutrient release capacity. Better nitrogen release was obtained by coating urea with pure poly (vinyl acetate), while the best nitrogen release capacity was found when coating urea with lignin and PVAc. It has also been shown that increasing the material's film thickness also delayed the nitrogen release period.

Biocomposites made of polylactide and cellulose acetate were used by El Assimi [139] to create a coated slow-release fertilizer. In this approach, PLA (polylactic acid) and CA (cellulose acetate) were used to coat diammonium phosphate (DAP) in a rotating pan. Using homogenizer machinery, CA and PLA were continually blended with a solvent combination to create the blend material. Comparing coated and uncoated DAP, the investigation's findings indicated that uncoated DAP had a faster potential for nutrient release. Further, it is noted that uncoated DAP released all of the nutrients within 1.5 hours, while the phosphorous release capacity of the material coated with cellulose acetate was significantly slowed down. It also shows that a larger PLA coating concentration increases the hydrophobic properties of the material. The PLA-CA (80:20) composition range with a 25 mm thickness demonstrated a superior release characteristic. It approached the European standard of slow release with 20 % phosphorus in water over the first 24 hours.

An et al. [140] studied with coated biochar-based fertilizers (CSRFs) synthesized through co-pyrolysis. The coating of BSRFs (biochar-based slow-release fertilizers) synthesized from the co-pyrolysis of $Mg_3(PO_4)_2$, bentonite, and cotton straw significantly improved the slow-release capacity. Fig. 9 illustrates the synthesis of CSRFs. According to the findings, coated CSRFs showed a 0.82 g/L phosphorus release capacity. In contrast, biochar-based slow-release fertilizers (BSRFs) showed a 1.98 g/L phosphorus release capacity over 30 days. According to indications, the P-release rate of CSRFs was around half that of BSRFs. Further biodegradability tests showed that CSRFs were better at breaking down than BSRFs and that 35.2 % of coated biochar-based slow-release fertilizers broke down within 60 days [140].

The cellulose extracted from waste hemp stalks was utilized to slow down the release of nutrients [141]. The process involved the conversion of cellulose into carboxymethyl cellulose (HCMC), followed by cross-linking with citric acid (CA) to produce a three-dimensional aerogel (HCMC-CA-aero). The aerogel demonstrated exceptional water absorption properties, with an 80 g/g capacity after 27 hours at a neutral pH. This behavior can be attributed to the aerogel's porous structure, which provided a large free volume between polymeric chains, numerous high flexibility, and hydrophilic groups. The synthesized material was consistently discharged with enclosed nutrient substances, urea and ammonium dihydrogen phosphate (ADP). After 40 hours of immersion in water, the HCMC-CA-aero@urea and HCMC-CA-aero@ADP exhibited nutrient release percentages of 48.4 % and 44.46 %, respectively. Meanwhile, when placed in soil, the nutrient release percentages were 62.28 % and 56.62 % after 120 hours,

indicating a high potential for soil conditioning. The Fickian diffusion and Higuchi model were observed to govern the release kinetics of both fertilizers, indicating a controlled release mechanism driven by dissolution and diffusion. Controlled-release fertilizers were developed using biodegradable chitosan and montmorillonite (MMT) nanoclays [142]. The incorporation of MMT within the chitosan hydrogels resulted in a significant increase in the overall release of phosphorous (P) and potassium (K), with a rise from 22.0 % to 94.9 % and 9.6–31.4 %, respectively, in comparison to the unmodified chitosan gel. The chitosan-MMT nanocomposite hydrogel demonstrated effective regulation of fertilizer release in soil. 55.3 % of the loaded fertilizer was released over 15 days, with a daily release rate of 2.8 percent. In the case of the conventional fertilizer powder, it was observed that 89.2 % of the fertilizer was leached out during the initial irrigation under identical conditions. The nanocomposites exhibited enhanced water absorbency, thereby improving water retention in the soil. Furthermore, the hydrogels composed of chitosan-MMT nanocomposites demonstrated a significant degradation rate of 57 % after being subjected to water swelling for 20 days.

### 8.2. *Inorganic form of slow-release fertilizers*

Many researchers have shown that coated fertilizers from inorganic materials effectively combat ordinary urea and other fertilizers' poor effectiveness [76] . Many inorganic minerals, including gypsum, sulfur, zeolite, bentonite, dolomite, and diatomite, are often employed in the coating process [156]. The Tennessee Valley Authority in the United States created the first coated slow-release fertilizer, sulfur-coated urea (SCU), tested in the rice field. Additionally, SCU is better than regular urea since it slows down the release of nutrients and speeds up their use [157,158]. Sulfur also contains acidic qualities that assist in balancing the alkalinity of the soil [1]. Gypsum has coating properties as well. Gypsum is better than sulfur for coating fertilizers since it does not change the pH of the soil and may easily provide plants with sulfate ions [159]. Zeolites possess distinctive chemical and physical characteristics. It is advantageous for agricultural soil because it can hold nutrients and water. Additionally, these zeolites have a capacity for exchanging cations. It has been claimed that nitrogen, phosphorous, and potassium fertilizers are coated with natural or modified zeolites [160].

Different urea-coating materials were created for the slow release of nutrients in research by Ridzwan et al. Mainly, sulfur was used as a coating material, but because sulfur is too fragile, this coating can easily peel off. Different inorganic coating materials, such as cement, gypsum, and zeolite, were used to coat urea in various combinations to avoid this problem. When these materials were combined, they were the most useful and cost-effective ones. The 1:1 ratio of sulfur to gypsum used for the coating urea showed good crushing strength and a reduced dissolve rate in water compared to the other combinations of ingredients.

Additionally, the performance of the substance is improved by covering the heated urea with molten paraffin wax. The outcome showed that gypsum might be used as a substitute coating material for urea [147]. Dolomite-alginate composite beads were created by Huang et al. as a potential phosphate fertilizer. A calcium cross-linked alginate hydrogel matrix was combined with ball-milled, ultrafine dolomite powders to create dolomite-alginate (DA) hydrogel beads to adsorb phosphate from wastewater. Then, the nutrients that were recovered are employed as slow-release fertilizers. It was shown that the DA beads released the nutrients gradually and sustainably; almost 90 % of the nutrients were released over 60 days [148]. Table 4 also includes a few more examples of organic and inorganic slow-release fertilizers and explains how they affect nutrient release in water and soil.

In another study, a dolomite phosphate rock (DPR)-based slow-release fertilizer for landscaping and agriculture was created by [149]. DPR contains magnesium, phosphorous, and calcium, potentially essential plant development elements. The primary goal of this research was to evaluate the agronomic effectiveness of DPR fertilizers for horticulture crops. DPR was adequate, with a lower proportion of 20–30 %. A zeolite-based nanocomposite that functions as a slow-release fertilizer was created by Lateef [150]. The synthesis of zeolite nanocomposite mainly involved two steps: first, zeolite was synthesized, and then nutrients (micronutrients and macronutrients) were added. In addition, studies were conducted to determine the release capacity in both soil and water. The findings showed that the release rate was almost similar in soil and water, except that the nutrient was released slightly higher in soil than in water. In another study, a slow-release nitrogen fertilizer based on surfactant-modified zeolite (SMZ) was developed [161]. This research aimed to look at the potential of using SMZ for slow-release N through anion exchange. The zeolite's nitrate-retention capacity was improved by adding a cationic surfactant (hexadecyltrimethylammonium). The results revealed that the nitrate-loaded SMZ showed a controlled release of nutrients in early greenhouse studies. So, according to various investigations, the controlled release characteristic may be attained by using inorganic materials. In the same way, the selection of the material should not result in the pollution of the land or the ecosystem. It is prudent to use a material that can be biodegradable so that this goal can be accomplished most effectively.

Coated urea was created using a dip-coating method and a covering material made from sustainable copolymer poly(S–M) (trash from the sulfur-petroleum and myrcene-citrus industries). The copolymer was first produced using a simple and efficient approach that did not require a solvent. The synthesis process involved only one step. According to the nitrogen test, the SRF with a coating thickness of 1733 μm releases just 16 % of its entire nitrogen after 4 days of incubation. In comparison, the pristine urea releases all its nutrients after 1 day. The soil burial test verifies the biodegradability of the copolymer. After 50 days of incubation in soil, the copolymer experiences a reduction in weight of about 18.25 %, confirming the degradation of the copolymer. The findings indicate that the recently created coated fertilizer adheres to the European Standard (EN 1326/2001) by releasing less than 15 % of its nutrients during the first 24 hours. [142].

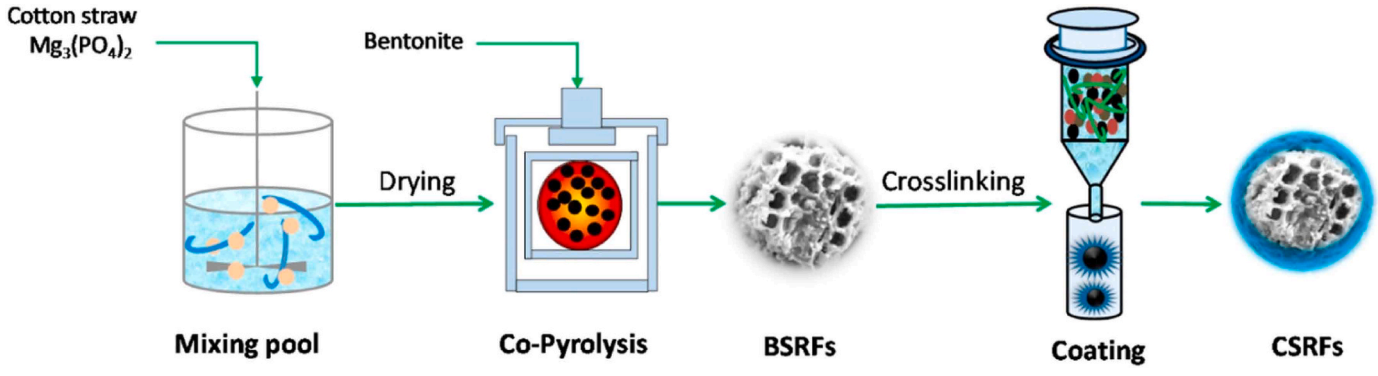


**Fig. 9.** Schematic illustration of the synthetic process of CSRF (reused from [140] with permission).

J. Liao et al. [151] synthesized a modified slow-release urea that is melt-coated and biodegradable using poly (butylene adipate-co-terephthalate) (PBAT) without the use of organic solvents. Poly(butylene adipate-co-terephthalate) (PBAT) underwent modification using titanium tris(dodecylbenzenesulfonate) isopropoxide (TDBSP), resulting in a reduction in both the molecular weight and crystallinity. Utilizing acetyl tributyl citrate (ATBC) as a plasticizer improved the flowability of the material, hence satisfying the special requirements of melt-coated urea. When applied as a coating, this mixture accounted for 18 % of the total mass of urea. The findings from the soil column leaching test demonstrated that the coated area had slow-release characteristics, as 80.09 % of the nutrients from the coated urea were released during 28 days. Using just one application of slow-release fertilizer that has been coated, the development of tobacco plants showed superior growth compared to that achieved by applying topsoil after 30 days in conventional cultivation techniques (using an equivalent quantity of fertilizer). Additionally, this approach reduced labor costs [151].

The study by P. Jumpapaeng et al., developed biodegradable nanocomposite hydrogels (BHM) by combining cassava starch (Cst), natural rubber (NR), polyacrylamide (PAM), and different amounts of montmorillonite (MMT) (ranging from 0 to 10 wt%). The hydrogels were fabricated using free-radical polymerization and semi-interpenetrating polymer network technology and were crosslinked with glutaraldehyde. The inclusion of MMT in BHM hydrogels substantially enhanced the biodegradability, tensile strength, and efficiency of nitrogen (N) release. BHM with MMT had the largest swelling ratio of 7074 % of the various formulations. Additionally, there were significant enhancements in mechanical strength, N release efficiency, and biodegradation rate compared to BHM without MMT. These results suggest a potential pathway for creating novel nanocomposite hydrogels using NR, Cst, and MMT components. These hydrogels could absorb and retain large amounts of water, possessed high strength, and underwent efficient biodegradation. Additionally, they exhibited prolonged slow-release properties and can maintain their structure in sustained conditions [152].

In a study by Yang et al. [153], a new slow-release fertilizer comprising nutritional nitrogen and phosphorus (PSNP) was synthesized using a biodegradable polymer. The PSNP material comprised a phosphate fragment and a urea-formaldehyde (UF) fragment formed by a solution condensation process. The controlled-release fertilizer PSNP gradually released nitrogen (N) and phosphorus (P) due to the degradation activity of microorganisms. After one month, only 34.23 % of the nitrogen and 36.91 % of the phosphorus had been released. Furthermore, the results of the soil incubation experiment and leaching experiment revealed that during the degradation of PSNP, UF fragments formed strong complexes with high-valence metal ions in the soil, inhibiting the fixation of phosphorus nutrients released during degradation, ultimately leading to a significant increase in the available phosphorus content in the soil. PSNP, a phosphate fertilizer with a larger molecular size and lower solubility than ammonium dihydrogen phosphate (ADP), had about double the accessible phosphorus (P) content in the 20–30 cm soil layer compared to ADP. The study shows a simple method for copolymerizing to produce PSNP, which exhibits exceptional slow-release properties for N and P nutrients. This advancement has the potential to support the progress of sustainable agriculture [153] significantly.

The poly(vinyl alcohol) (PVA)/sodium alginate (SA) polymer membranes were used as environmentally benign and biodegradable coverings for SRFs [154]. The process included applying a polymer layer to the urea granules and creating polymer-coated urea (PCU) granules. Membranes were prepared using varied weight ratios of PVA/SA (9:1, 8:2, 7:3) and crosslinked using glutaraldehyde as the crosslinking agent, which was later crosslinked with a $CaCl_2$ solution to generate the final membrane. The membrane with the least weight ratio of PVA/SA, exhibited the most excellent hydrophilicity. The membrane exhibited biodegradation ratios ranging from 44 % to 60 % during 90 days, suggesting their biodegradability. The PVA/SA membranes produced were environmentally benign and capable of decomposing, making them viable substitutes for SRF coatings [154].

Z. Yang et al. [155], used three kinds of degradable materials, namely poly(vinyl alcohol) (PVA), alkali lignin (AL), and corn starch (CS), to create a mulch film that had a slow-release fertilizer function (MSRF). The material had excellent water resistance, maintaining its morphology for 50 days. It exhibited a high water absorption capacity of 300 % and efficiently released urea, with a cumulative release of 70.63 % within 30 days. The rapid plant growth studies provided evidence of the exceptional performance of the MSRF, which resulted in a reduction of almost 70 % in the quantity of fertilizer used. The combination of the aggregation capabilities of AL, the hydrogen bonding between the AL, CS molecules, and PVA, and the chemical cross-linking (chemical bonding) between the AL and PVA/CS molecular chains were responsible for these efficiencies. This technique provided an environmentally friendly and effective method for preparing and applying mulch while also providing a delayed release of fertilizer [155].

An interpenetrating polymer network (IPN) was synthesized using a one-pot method to coat urea with castor oil in a study by [82] . In order to enhance the mechanical properties of controlled-release fertilizer (CRF) materials derived from bio-oil, sulfur (S) was employed to synthesize polyurethane interpenetrating polymer networks. The findings indicate that the cumulative nutrient release of CSUs (Coated Slow--Release Urea) over 56 days is below 10 %, thereby exhibiting the lowest nutrient release proportion among CRFs formulated utilizing oil-based constituents. In the context of the limit state test for CSU, it was observed that upon increasing the proportion of PMDI (diphenylmethane diisocyanate) to 33.33 % and subjecting it to a water soaking period of 210 days, the nutrient residue in CSU remained above 20 % and it represents a relatively prolonged nutrient release longevity for oil-based materials.

## 9. Conclusion and the way forward

There is no denying that the present agricultural practices of overuse of fertilizers and over-exploitation of ground and surface water to attain food security for the growing population on the earth are unsustainable. Conventional chemical fertilizers, being water soluble, release nutrients at a much faster rate than that required by plants. As a result, a significant amount of the fertilizer is wasted through runoffs and leachates from the agricultural field, which causes nutrient overloading, leading to eutrophication and related environmental problems. The economic burden of such a waste of resources on all the stakeholders is also enormous. Therefore, the development of innovative environment-friendly fertilizers is emerging as a future trend to increase agricultural productivity while minimizing worldwide sustainability issues. The worldwide focus on enhancing agricultural sustainability and securing a sustainable food supply has led to significant attention on the development of slow-release and controlled-release fertilizers, state-of-the-art information about which were discussed in this article, including its process of synthesis, nutrient utilization efficiency, and benefits in modern and eco-friendly farming. Slow-release fertilizers provide plants with a steady supply of nutrients in the root zone, which is often commensurate with the demand pattern of the plants, thus increasing their efficiency and leading to the lowering of the cost of inputs for crop production. The hydrophilicity of these new-generation fertilizers also helps to preserve water at the root zone and release it as per the plants' needs, ultimately promoting the efficient and wise utilization of water. Recent developments in slow-release fertilizers open up new possibilities for cost-effective modern farming. For long-term sustainability, it is best to use slow-release fertilizers based on biodegradable material to avoid the build-up of environmentally harmful polymers used for the coatings.

Future research should focus on using biopolymers as a framework and regulating the discharge of fertilizers. Biopolymers are abundant, eco-friendly, capable of undergoing biodegradation, and can reduce

**Table 4**
Nutrient release behaviour of Slow-release Fertilizers.

| Type of fertilizer | Nutrient | Nutrient release performance in water | Nutrient release performance in soil | References |
|---|---|---|---|---|
| **Organic slow-release fertilizers** | | | | |
| • Double-coated slow-release fertilizer | Urea | - | The potato-SAP coated fertilizer indicated a better slow-release property with a release amount of 40% in 24 h and could steadily release the nutrient for an extended period (70% at 96 h). | [79] |
| • Urea-impregnated HAP encapsulated by lignocellulosic biomass-extruded composites | Urea | After 30 days of complete immersion in water, urea-modified-HAP encapsulated by SCB biopolymer, urea-modified-HAP encapsulated by cellulose fibers, and urea-modified-HAP encapsulated by lignin fibers were found to have released only about 59, 45.48, and 21.64%, respectively. | - | [124] |
| • CS-PEG-MMT 5%-PW | Diammonium phosphate | The total release of phosphorous in water was extended to 16 hours by using double-coated DAP granules (CS-PEG-MMT 5%-PW). | Double-coated DAP granules (CS-PEG-MMT 5%-PW) nutrient release rate at first 30 days is less than 40%. | [137] |
| • Starchacetate/glycerol/polyvinyl alcohol biocomposites | Diammonium phosphate (N and P release) | Coated DAP (CF-3) with single and double layers reached the equilibrium state to release the profile at 200 and 270 min, respectively. Further, the N release from coated DAP (CF-3) was determined to be 2.4 and 3.2 times higher than uncoated DAP, and the material is coated with single and double layers, respectively. | - | [72] |
| • Slow-release fertilizer based on lignin and poly (vinyl acetate) bioblend | Urea | The greatest nitrogen release time was observed by urea coated with both lignin and PVAc in the mass ratio of 25:75 with the time-release up to 720 ± 4.5 min. | - | [138] |
| • Slow-release fertilizer by using polylactide and cellulose acetate biocomposites as a coating material | Diammonium phosphate | The composition range of PLA-CA (80:20) with a thickness of 25 μm proved a better release characteristic and approached the European Standard of slow-release with a release of 20 % of phosphorus in water during the first 24 h. | - | [139] |
| • Coated biochar-based fertilizer (CSRFs) | $Mg_3(PO_4)_2$ | The results showed that the release capacity of phosphorus is 1.98g/L for biochar-based slow-release fertilizers (BSRFs) within 30 days period, while the release capacity of phosphorus from coated biochar-based slow-release fertilizers (CSRFs) is 0.82g/L. | - | [140] |
| • HCMC-CA-aero | Urea and ammonium dihydrogen phosphate (ADP) | Following a 40-hour immersion in water, the HCMC-CA-aero@urea and HCMC-CA-aero@ADP demonstrated corresponding 48.4% and 44.46% nutrient release percentages. | The percentage of nutrient release was 62.28% and 56.62% at the end of a 120-hour period. | [141] |
| • Chitosan-MMT nanocomposite hydrogels | NPK | In water: 71 % N,61 % P, 15 % K in 12 days. | In soil:55 % NPK in 15 d | [142] |
| • Starch-g-Poly(AAm) (SBSAPs) | Urea | The urea release capacity of SBSAPs in water is less than 15% within one day. The release rate after 30 days exceeded 80%, and the release lasted for more than 45 days. | - | [143] |
| • Starch-g-poly(acrylic acid-co-acrylamide) based slow-release fertilizer with natural char nanoparticles (NCNPs) | Urea | This slow-release fertilizer formulation showed a good urea release capacity in water, 70 % of nitrogen released during 21 days. | The nitrate release rate in the soil for pure urea was measured to be 591.8 mg/L, and the starch-g-poly (acrylic acid-co-acrylamide)/ NCNPs/Urea reduced the release rate of N up to 49.5 mg/L. | [144] |
| • Modified cellulose (CCDEUs-poly (AA)/urea) as a slow-release fertilizer | Urea | Urea release capacity in water is 40.1%, released during 10 hours. | Results indicated that only 14.2% of urea was released after five days, while during 5–30 days, 90.4% of urea was released. | [88] |
| • SC-g-PAA/ PAM/Urea | Urea | The cumulative nutrient release of SC-g-PAA/PAM/Urea was 2.6%, 8.6%, and 82.4% within 10, 30, and 480 min, respectively. | - | [145] |
| • MSP-g-AA/PVA-APP | The ammonium polyphosphate (APP) is used to supply nitrogen and phosphorus nutrients. | - | The cumulative Nitrogen and Phosphorus release rates of MSP-g- AA/PVA-APP were 55.1 % and 47.3 % after 30 days in soil, respectively. | [87] |
| • Corncob-g-Poly(AAm)/Bent/PVP/ urea | Urea | - | The urea release rate in the soil is 56.6% after 30 days. | [146] |

(*continued on next page*)

**Table 4** (*continued*)

| Type of fertilizer | Nutrient | Nutrient release performance in water | Nutrient release performance in soil | References |
|---|---|---|---|---|
| • Hydrogel-biochar composite based on pine resin as a carrier for controlled release | N-P-K | The controlled release ratio of N-P-K nutrition in distilled water was found to be less than 85%. | The developed LCBH-SRF exhibited below 90% release of N-P-K in soil. | [130] |
| • Slow-release NPK fertilizer that is derived from biochar | N-P-K | - | Approximately 47.60–58.27% of nitrate ions ( $NO_3^-$ ), 47.84–65.40% of ammonium ions ($NH_4^+$),), and 58.05–59.07% of potassium oxide ($K_2O$) were successfully extracted from a column depth ranging from 40 to 50 cm during this process. This suggests that the SRF efficiently retains the nutrients in the upper layer of soil and restricts the potential for leaching. | [131] |
| • A secondary and micronutrient enriched nano-fertilizer | Secondary and micronutrient | A study on nutrient release patterns revealed that after 90 days, the concentration of calcium ions ($Ca^{2+}$) released varied between 87.4% and 90.7%, magnesium ions ($Mg^{2+}$) ranged from 81.8% to 85.3%, sodium ions ($Na^{+}$) ranged from 96.2% to 99.1%, iron ions ($Fe^{2+}$) ranged from 2.8% to 5.2%, and zinc ions ($Zn^{2+}$) ranged from 0.5% to 1.6%. | - | [132] |
| • Lignin polymers derived from various plant biomass as coating materials for P fertilizers | Phosphate | The uncoated TSP revealed a full release of 100% of P after three days. On the other hand, TSP@L-OP has released 16.9%, whereas TSP@L-BS has released 33.4%. | - | [133] |
| • SRF pellets formulated with different mass ratios of biochar and urea | Urea | - | The study indicates that biochar-based slow-release fertilizers (SRFs) have the capacity to decrease the leaching of NO3− from agricultural soils. | [134] |
| • Biodegradable composite hydrogel | Urea | The GCPU composite hydrogel demonstrates a progressive release of nutrients, with rates of 20%, 70%, and 86% during time intervals of 10 minutes, 180 minutes, and 900 minutes, respectively. | - | [135] |
| • UCNF | Urea | The urea loaded in UCNF released at a very slow rate, taking around 30 days time. | - | [136] |
| **Inorganic slow-release fertilizers** | | | | |
| • Different urea-coating materials | Urea | Sample C5 was formulated based on the same proportion of sulfur and gypsum plaster and was identified to have the best efficiency of 13.8%. | - | [147] |
| • Dolomite–alginate composite beads | Phosphate | About 90% of the adsorbed phosphate wasreleased over 60 days. | - | [148] |
| • DRP (Dolomite phosphate rock) | Phosphate and other minerals | - | Dolomite phosphate rock material with a lower proposition of 20-30% is demonstrated to be optimal in delivering nutrients for plant growth. | [149] |
| • Zeolite-based nanocomposite | Macronutrients and micronutrients | Initially, the release is a little faster, which decreases with the period of time. | It exhibited the same trend as was observed in the case of tap water, except that the concentration of nutrients released is higher than that in water. | [150] |
| • Sulfur and myrcene (S–M) | Urea | Urea release concentration was 78% in 30 days. | - | [142] |
| • Modified biodegradable poly (butyleneadipate-co-terephthalate) (PBAT) based melt-coated slow-release urea | Urea | - | The results of the soil column leaching test demonstrate that the coated area had characteristics of slow-release, with 80.09% of the nutrients from the coated urea being released over a period of 28 days. | [151] |
| • Biodegradable nanocomposite hydrogels (BHM) | Urea | - | The rates of urea release from the formulations FWBHM0, FWBHM3, FWBHM5, and FWBHM10 after 8 and 30 days are as follows: 31.83%, 23.60%, 22.04%, 18.46% and 65.38%, 51.51%, 49.59%, 39.78%, respectively. The findings suggest that the inclusion of MMT in the BHM nanocomposite hydrogels (namely the FWBHM3-FWBHM10 formulations) may significantly slow down the release of urea. | [152] |
| • Slow-release fertilizer comprising nutritional nitrogen and phosphorus (PSNP) | Nitrogen and phosphorous | - | The controlled-release fertilizer PSNP progressively releases nitrogen (N) and phosphorus (P) nutrients via the action of microorganisms. After a duration of one month, a mere 34.23% of the nitrogen and 36.91% of the phosphorus were released. | [153] |

(*continued on next page*)

**Table 4** (*continued*)

| Type of fertilizer | Nutrient | Nutrient release performance in water | Nutrient release performance in soil | References |
|---|---|---|---|---|
| • PVA)/sodium alginate(SA) polymer membranes as eco-friendly and biodegradable coatings for SRFs | Urea | - | The fractional release of the three PCU granules on day 30 is, in that order, 93.77%, 94.64%, and 97.07%. This change is consistent with membrane water absorption with the SA content. The PCU with the PC3 membrane has the lowest fractional release, measuring at 89.33%. | [154] |
| • Mulch film with a slow-release fertilizer function (MSRF) | Urea | The use of the MSRF with 10% AL resulted in a delay of about 120 minutes in the release of 64% of urea. | The Re (%) of MSRF with 10% AL in soil was 70.63% during a period of 30 days. | [155] |

costs for the raw ingredients needed to produce SRF. When degraded through composting, they enhance the organic carbon content of the soil, enhance the soil quality, and supply essential nutrients to plants [162]. When developing new slow-release fertilizers, it is vital to consider using naturally occurring raw materials that break down slowly to promote sustainability. However, using natural biopolymers such as cellulose and starch is difficult due to their sensitivity to microbes, weak durability, and quick breakdown characteristics through hydrolysis. Consequently, this often leads to ineffective slow-release properties. Therefore, substantial endeavors should be undertaken to manufacture highly efficient bio-based coating materials, such as bio-sourced polyols for bio-polyurethane coatings and hydrophobic modifications. It is essential to control the speed at which they break down naturally and how long they last, considering the soil and weather conditions and the nutritional requirements of crops throughout their development stage. Such a controlled release is necessary to meet their specific demands and to be able to compete with the majority of resin-based commercial polymer-coated fertilizers now available.

Moreover, there is a need for a more precise evaluation of the economic benefits of using polymer-coated fertilizer in a single application. Ideally, this assessment should be conducted in various field settings and include a cost/benefit ratio analysis to provide a more realistic comparison with conventional fertilizers. In addition, combining polymer-coated fertilizer with sophisticated agronomical technology and best agricultural practices allows for the optimal use of agronomic and environmental benefits [163].

Establishing standardized techniques at national and global levels is crucial to accurately evaluate the rate at which SRF/CRF releases nutrients under different environmental conditions. This is essential for maintaining the reliability and consistency of these products. This would provide a standardized approach for assessing the efficiency of SRF/CRF, enabling meaningful comparisons across different research studies and products. Bio/nanomaterials, including agricultural waste, nano clays, plant oil-based polymers, and degradable polymer nanoparticles (such as nano-chitosan, nano-lignin), possess distinctive characteristics that make them highly suitable for use as nano/microcarriers in SRF/CRF. Nevertheless, a lack of studies exists on using nanotechnology in the production of SRF/CRF, which needs additional analysis and development.

## CRediT authorship contribution statement

**Priya E:** Writing – original draft, Investigation. **Pradip K Maji:** Writing – review & editing, Supervision. **Sudipta Sarkar:** Writing – review & editing, Supervision.

## Declaration of Competing Interest

None.

## Data Availability

No data was used for the research described in the article.

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